Determination of priority organic substances in surface water containing suspended particulate matter by disk solid phase extraction

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Und jedem Anfang wohnt ein Zauber inne,
Der uns beschützt und der uns hilft, zu leben.

Hermann Hesse

Abstract

The European Water Framework Directive (WFD, Directive 2000/60/EC) requires an extensive monitoring of surface water on priority and priority hazardous substances mentioned in Directive 2008/105/EC. Many of these substances can sorb strongly on suspended particulate matter (SPM) due to their hydrophobic character. Therefore, the so called whole water sample, the water sample including solid matter, has to be investigated. The usually used sample preparation methods, such as liquid-liquid extraction (LLE) or solid phase extraction (SPE), are affected by SPM by the formation of emulsions, insufficient extraction of particle-bound analytes or plugging. Consequently, SPM and water sample are often separated, e.g., by filtration, and analysed separately. This approach is associated with a high expenditure of time and work. An alternative may be the use of SPE disks. They have an enhanced diameter compared to SPE cartridges and therefore tend less to plugging. Therefore, an extraction of the whole water sample may become possible in one step.

After a first extensive investigation of the occurrence of residual water and its effects in disk SPE to reduce analytical interferences, a multi-component trace analysis of 54 organic xenobiotics in surface water by SPE disk/gas chromatography-mass spectrometry (GC-MS) was developed and validated considering the requirements of the WFD and its following directives. The developed procedure allows the determination of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), organochlorine pesticides (OCPs) and other pesticides in 1 L water containing up to 1000 mg SPM/sample. The SPE disk sample preparation is combined with two GC-MS methods, differing only in their injection modes to cover a large concentration range. This large concentration range is due to the high number of investigated analytes and the targeted limits of quantification (LOQs), which are associated with the environmental quality standard (EQS) values. The annual average - EQS values in surface water are between 0.0005 and 2.4 µg/L for the investigated analytes. The reached LOQs up to 0.1 ng/L (S/N = 6:1) are lower compared to numerous methods described in literature and for the first time a SPE disk method coupled to large volume injection/GC-MS method was validated. The overall processing time is about 2.5 h/sample, including both GC-MS methods. For 85 % of the investigated analytes all requirements of WFD were fulfilled by the described SPE disk/GC-MS procedure. In future an improvement of the LOQs could be achieved for example by the increase of the sample volume of 2 L or more or by the use of more sensitive detection methods such as GC-MS/MS.

Kurzfassung

Die europäische Wasserrahmenrichtlinie (WRRL, Direktive 2000/60/EG) fordert eine intensive Überwachung von Oberflächengewässer auf die in der Direktive 2008/105/EG genannten prioritären und prioritär gefährlichen Stoffe. Vieler dieser Substanzen können wegen ihres hydrophoben Charakters stark an Schwebstoffen (SPM) sorbieren. Daher muss die sogenannte Gesamtwasserprobe, also die Wasserprobe einschließlich der darin befindlichen Feststoffe, untersucht werden. Die üblicherweise verwendeten Probenvorbereitungsverfahren, wie etwa die flüssig-flüssig Extraktion (LLE) oder die Festphasenextraktion (SPE), werden durch die Bildung von Emulsionen, unzureichende Extraktion der partikelgebundenen Analyten oder Verstopfungen auf Grund der SPM gestört. Folglich werden SPM und Wasserprobe häufig voneinander getrennt, z.B. durch Filtration, und separat analysiert. Dieser Ansatz ist mit einem hohen Zeit- und Arbeitsaufwand verbunden. Eine Alternative können Festphasenextraktionsscheiben (SPE disk) sein. Sie besitzen einen größeren Durchmesser als SPE Kartuschen und neigen daher seltener zu Verstopfungen. Dadurch kann eine Extraktion der Gesamtwasserprobe in einem einzigen Verfahrensschritt ermöglicht werden.

Nach erstmaliger ausführlicher Untersuchung des Auftretens von residualem Wasser und seinen Auswirkungen auf die Festphasenextraktion mit SPE disks, um analytische Störungen zu reduzieren, wurde eine Multikomponentenmethode zur Spurenanalyse von 54 organischen Xenobiotika in Oberflächenwasser mittels SPE disk/Gaschromatographie-Massenspektrometrie (GC-MS) unter Berücksichtigung der WRRL und ihrer Folgerichtlinien entwickelt und validiert. Das entwickelte Verfahren ermöglicht die Bestimmung von polycyclischen aromatischen Kohlenwasserstoffen (PAK), polychlorierten Biphenylen (PCB), polybromierten Diphenylethern (PBDE), Organochlorpestiziden (OCP) und anderen Pestiziden in 1 L Wasser mit SPM-Gehalten von bis zu 1000 mg/Probe. Dazu wurde die SPE disk Methode mit zwei GC-MS Methoden kombiniert, die sich nur in ihren Injektionsmodi unterscheiden, um einen großen Konzentrationsbereich abzudecken. Der große Konzentrationsbereich ist auf die große Anzahl der untersuchten Analyten und den anvisierten Bestimmungsgrenzen (BG), welche mit den Werten der Umweltqualitätsnorm (UQN) verbunden sind, zurückzuführen. Die Jahresdurchschnittswerte der UQN für die untersuchten Analyten in Oberflächenwasser liegen zwischen 0,0005 und 2,4 µg/L. Die erreichten BG von bis zu 0,1 ng/L (S/N = 6:1) sind niedriger als die vieler in der Literatur beschriebener Methoden und erstmalig wurde eine mit SPE disk gekoppelte Large Volume Injektion/GC-MS Methode validiert. Die Gesamtanalysenzeit beträgt ca. 2,5 h/Probe, einschließlich beider GC-MS Methoden. Für 85 % der untersuchten Analyten können alle Anforderungen der WRRL mit der beschriebenen SPE disk/GC-MS Prozedur erfüllt werden. Eine Verbesserung der Bestimmungsgrenze kann in Zukunft zum Beispiel durch die Erhöhung des Probenvolumens, um 2 L oder mehr, oder durch die Verwendung sensitiverer Detektionsmethoden wie der GC-MS/MS, erreicht werden.

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List of abbreviations

a	y-intercept
AA-EQS	Annual average environmental quality standard
alpha-HCH	alpha-hexachlorocyclohexane
ASE	Accelerated solvent extraction
b	Slope
BDE 28	2,4,4'-tribromodiphenyl ether
BDE 47	2,2',4,4'-tetrabromodiphenyl ether
BDE 99	2,2',4,4',5-pentabromodiphenyl ether
BDE 100	2,2',4,4',6-pentabromodiphenyl ether
BDE 153	2,2',4,4',5,5'-hexabromodiphenyl ether
BDE 154	2,2',4,4',5,6'-hexabromodiphenyl ether
BG	Bestimmungsgrenzen, engl. LOQ
beta-HCH	beta-hexachlorocyclohexane
C	Carbon
c	Concentration
°C	Degree Celsius
c.a.c.	Constant analyte concentration
C_8	Octa carbon chain,C_8H_{17} alkyl group
C_{18}	Octadecyl carbon chain, $C_{18}H_{37}$ alkyl group
CEN	European Committee for Standardization
CIS	Cooled injection system
CLND	Chemiluminescent nitrogen detector
cm	Centimetre
CRMs	Certified reference materials
D	Deuterium
DAD	Diode area detector
delta-HCH	delta-hexachlorocyclohexane
dH	Degree of German hardness
DVB	(Styrene) divinylbenzene
DVB-RPS	Sulfonated DVB material
ECD	Electron capture detector

ED	Multi-electrode electrochemical detector
EI	Electron impact ionization
EPA	Environmental Protection Agency
EQS	Environmental quality standards
ESP	High-flow pneumatically assisted electrospray
eV	Electron volt
FAAS	Flame atomic absorption spectrometry
FAB	Fast atom bombardment
FD	Fluorescence detection
FID	Flame ionization detected
FLD	Flourescence detector
FTD	fFame thermionic detector
FPD	Flame photometric detection
FT-IR-MS	Fourier transform infrared mass spectrometer
gamma-HCH	gamma-hexachlorocyclohexane, lindane
GC	Gas chromatography
GCB	Graphitized carbon black
GC-MS	Gas chromatography-mass spectrometry
h	Hour
H	Hydrogen
hc	High capacity
HLB	Hydrophilic/lipophilic balanced
H_2O	Water
HPLC	High performance liquid chromatography
HR	High resolution
HRMS	High resolution mass spectrometry
IS	Internal standards
IUPAC	International Union of Pure and Applied Chemistry
k	k-Factor
L	Litre
LC	Liquid chromatography
LD	Liquid desorption
LFER	Linear free energy relationships
LLE	Liquid-liquid extraction

LLME	Liquid–liquid microextraction
LOD	Limit of detection
log K_{OC}	Partition coefficient between organic carbon and water
log $K_{acetone - air}$	Partition coefficient between organic carbon and water
Lot. No.	Lot number
LOQ	Limit of quantification
LSER	Linear solvation energy relationship
LVI	Large volume injection
m	Meter
MAE	Microwave-assisted extraction
MALDI	Matrix-assisted laser desorption/ionization
MASE	Membrane-assisted solvent extraction
MEKC	Micellar electrokinetic chromatography
MEPS	Microextraction by packed sorbent
mg	Milligram
µg	Microgram
MISPE	Molecularly imprinted solid-phase extraction
µL	Microliter
mL	Millilitre
µm	Micrometer
mm	Millimetre
MMLLE	Microporous membrane liquid–liquid extraction
µS	Micro-Siemens
min	Minute
MPS	Multi-purpose-sampler
MS	Mass spectrometry
MSD	Mass selective detector
MWCNT	Multi wall carbon nano tubes
m/z-ratio	Mass to charge ratio
n	Number of measurements
n.d.	Not detected
ng	Nanogramme
NPD	Nitrogene phosphorus detector
OCP	Organic chlorinated pesticide

OGewV	Oberflächengewässerverordnung, German implementation of WFD
o,p'-DDT	2,2-bis(o,p-chlorophenyl)-1,1,1-trichloroethane
PAH	Polycyclic aromatic hydrocarbon
PAK	Polycyclischen aromatischen Kohlenwasserstoff, engl. PAH
PBDE	Polybrominated diphenyl ether
PCB	Polychlorinated biphenyl
PMDS	Polydimethylsiloxane
pH	pH value
pH_{sample}	pH value of the sample
PLE	Pressurized liquid extraction
PTFE	Polytetrafluoroethylene
p,p'-DDE	p,p'-(dichlorodiphenyl)-2,2-dichloroethylene
p,p'-DDT	p,p'-dichlorodiphenyltrichloroethane
p,p'-TDE	p,p'-(dichlorodiphenyl)dichloroethane
PTV	Programmable temperature vaporizer
r	Correlation coefficients
Ref.	Reference
RIA	Radioimmunoassay
RSD	Relative standard deviation
RTP	Room-temperature phosphorimetry
SALDI	Surface-assisted laser desorption ionization
SAX	Strong anion exchange
SCX	Strong cation exchange
SBSE	Stir bar sorptive extraction,
SD	Standard deviation
SDS	Sodium dodecyl sulphate
SEE	Standard error estimation ~ SD
SFE	Supercritical fluid extraction
SIM	Selected ion monitoring
S/N	Signal to noise ratio
SPE	Solid phase extraction
SPED	Solid phase derivatization
SPM	Suspended particulate matter
SPME	Solid phase micro extraction

$t_{(N-1,\ 99\ \%)}$	Student's t-value at a 99 % confidence level and N−1 degree of freedom
TLC	Thin layer chromatography
TD	Thermal desorption
UHPLC	Ultra high performance liquid chromatography
UK	United Kingdom
UQN	Umweltqualitätsnorm, engl. EQS
UV	Ultra violet detector
v/v	Volume to volume ratio
VIS	Visible
V_{sample}	Sample volume
VS	Volumetric standard
WFD	Water Framework Directive, Directive 2000/60/EC
w/w	Weight to weight ratio
w/v	Weight to volume ratio
x	Concentration
y	Signal
$y = b \bullet x + a$	Equation of calibration
-	Not determinable or no information available

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1 General introduction

"*Water is not a commercial product like any other but, rather, a heritage which must be protected, defended and treated as such* [1]." This is the first sentence of the European Directive 2000/60/EC, called Water Framework Directive (WFD), introduced in 2000. Its aim is to establish a transnational framework in the European Community in the field of water policy to obtain and improve the water quality [1]. Therefore, the members of the European Community established a suitable management and protection system for fresh water resources, to achieve a good surface water status in 2015 (Figure 1.1).

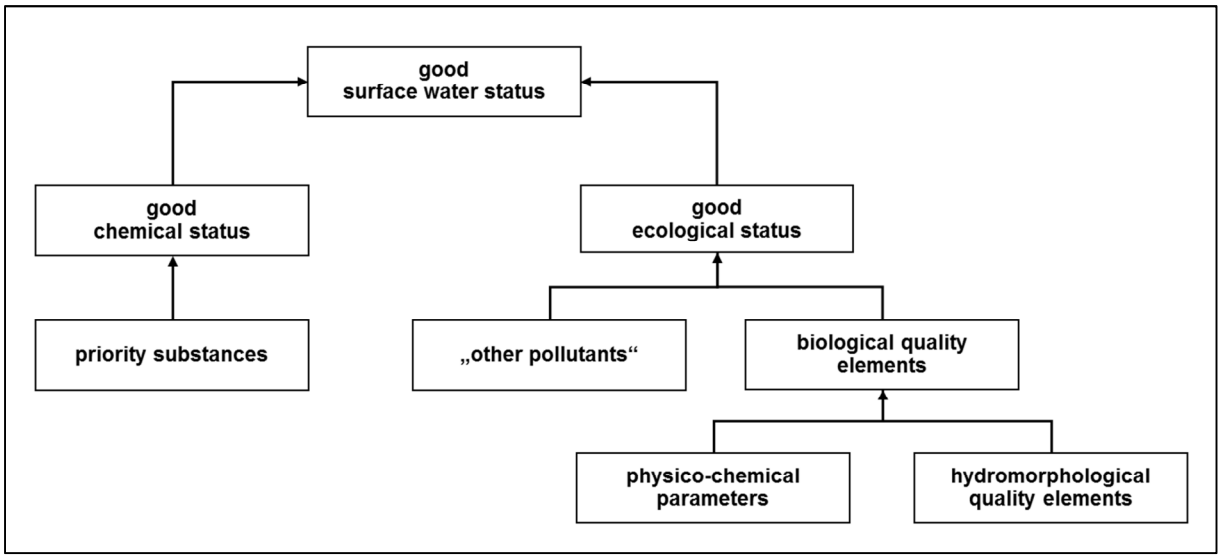

Figure 1.1: Overview on the attainment of a good surface water status [1, 2]

A good surface water status is defined by the ecological and chemical status of a surface water. The ecological status expresses the quality of the structure and function of an aquatic ecosystem and is described by the biological quality of a water body, influenced by pollutants. The biological quality consists of physico-chemical and hydromorphological elements and a good ecological status is achieved when the biological quality elements of a water body only slightly deviate from those of an anthropogenically unaffected water body (Figure 1.1) [1].

For the attainment of a good chemical status, a list of priority and priority harzardous substances with corresponding environmental quality standards (EQS) values has been defined (Figure 1.1). The identification of priority substances and their EQS values is based on a scientific risk assessment procedure based on a combined approach of monitored and modelled data by verification, if available, with hazard and risk assessments and derived levels of concern [3, 4].

The list of relevant priority substances is completed on the national level for example for polychlorinated biphenyls (PCBs) in the German implementation of the WFD, called Oberflächengewässerverordnung (OGewV). A good chemical status is achieved, when the concentrations of pollutants do not exceed EQS values. Thus the emission of these substances into the environment has to be reduced or stopped until their concentrations are below their EQS values [1].

Consequently, a good surface water status is reached, if both a good ecological and a good chemical status is present [1, 2]. Hence a continuous monitoring of water resources on its chemical, biological and environmental quality has to be realized, after a first extensive data collection and definition of EQS [1, 2].

For the analysis of organic priority and priority harzardous substances the water samples including the suspended particulate matter (SPM), called whole water sample (Figure 1.2), have to be investigated [1, 2, 5].

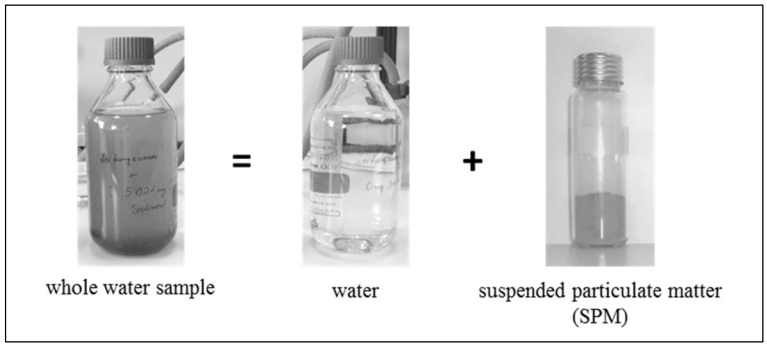

Figure 1.2: Scheme of whole water sample

This is due to partly substantial sorption of these substances on SPM [2] depending on their hydrophobicity. Sorption is for example relevant for polycyclic aromatic hydrocarbons (PAHs) [2, 6]. Accordingly, the SPM has also to be covered in analysis [2]. Furthermore, for the used analytical methods technical specifications and minimum performance criteria are defined. For example, the measurement uncertainty shall be equal or below 50 % (k = 2) estimated at the relevant EQS and the limits of quantification (LOQ) may not exceed 30 % of the associated EQS value [1, 7].

Consequently, analytical methods are required, which (I) fulfil the mentioned requirements of the WFD such as the analysis of the whole water sample and achievement of the minimum performance criteria, including the partly very low LOQs down to 0.00006 µg/L (30 % of annual average (AA) - EQS values for surface water of tributyltin compounds), (II) minimize the expenditure of work, time and money and (III) allow a high sample throughput.

Most available analytical methods have not been validated for water samples containing higher amounts of SPM [6, 8]. SPM in water samples affects the liquid-liquid extraction (LLE) or the solid phase extraction (SPE) and induces for example insufficient extraction of particle-bound analytes, formation of emulsions or plugging [6, 9]. Thus, SPM is often separated from the water sample and analysed separately. The simplest way for separation is filtration [6]. Whether the water sample is analysed as a whole or the aqueous phase and the SPM are analysed separately is not regulated by the WFD [2]. As already mentioned in a review on the investigation of the whole water sample, it is not advisable to analyse exclusively the aqueous phase or the SPM [6]. Although an existing rule of thumb states that substances with a partitioning coefficient of $\log K_{octanol - water} < 3$ are mainly present in the aqueous phase, no general rule can be fixed, which phase should be analysed [6]. Therefore, the approach to analyse only one phase induces underestimation of analyte concentrations due to nonnegligible presence of analytes in the unconsidered phase [8] and the results are strongly influenced by the used separation technique [6]. The separation technique defines the separated particle size and thus which fraction of particles is considered during subsequent analysis. The separation of both phases and the separated analysis are associated with a higher expenditure of time and work and increases the risk of contamination [6]. Furthermore, only few standard methods exist for sediment analysis [10, 11]. Consequently, validated methods for the analysis of the whole water sample are needed.

Figure 1.3: SPEC C_{18} AR SPE disk from Varian without and with suspended particulate matter (SPM; from the left to the right)

An alternative to the mentioned sample preparation techniques can be disk SPE. Besides high capacities, less channeling and high flow rates, SPE disks tend less to plug due to the enhanced diameter compared to SPE cartridges and allow the extraction of large water samples including SPM. Hence, SPM has not necessarily to be separated and the whole water sample can be analysed in one process [6, 12, 13]. During the extraction of the water sample containing SPM, the SPM remains on top of the SPE disk (Figure 1.3). After a subsequent drying step, the analytes can be desorbed from the SPE sorbent and the SPM by an organic solvent in one step. Then the extract can be analysed directly or after further treatment such as a concentration step.
This approach saves time and work, due the analysis of the whole water sample in one process. Furthermore, the European Committee for Standardization (CEN) expressly requires to check the analysis of the whole water sample by disk SPE for several substance groups as for example PAHs, polybrominated diphenyl ethers (PBDEs) and organic chlorinated pesticides (OCPs) and to compare it with alternative methods [6].

The aim of this work was the development of a multi-compound trace analytical method for priority and priority hazardous organic compounds in surface water containing SPM considering the requirements of the WFD and its following directives based on disk SPE.
Special challenges were (I) analysis of the whole water sample including SPM in a single procedure, (II) achievement of the partly very low EQS values, (III) coverage of a wide concentration range due to the largely varying EQS values of the many analytes, (IV) fulfilment of the performance criteria of the WFD considering minimization of expenditure of time and work.

At the beginning, an overview of existing methods and approaches for analysis of organic substances in water using SPE disks is given since so far this has not been described in literature (Chapter 2). It turns out that the causes and consequences of residual water, which remains in SPE disks after sample extraction despite a drying step, are hardly investigated although the residual water influences all following process steps including the instrumental analysis. Thus, this point was investigated for the first time in a systematic manner (Chapter 3). Based on the reported findings a multi-compound trace analytical method of organic substances in surface water containing SPM by disk SPE/gas chromatography-mass spectrometry (GC-MS) was developed (Chapter 4). The method was validated for 54 organic xenobiotics, covering the substance groups of PAHs, PCBs, PBDEs, OCPs and other pesticides considering the list of priority and priority hazardous substances of the WFD and was finally compared with LLE and Soxhlet extraction. The AA-EQS values for surface water of the investigated analytes range from 0.0005 to 2.4 µg/L. To improve the LOQs with a minimum of work and time to achieve all LOQs required for fulfilment of the WFD, in subsequent investigations the developed SPE disk method was combined with large volume injection (LVI)/GC-MS (Chapter 5). Although this approach is simple, such a method was never validated before.
At the end, the major conclusions from the work on the disk SPE approach for the analysis of the whole water sample are summarised and an outlook on further investigations is given (Chapter 6).

1.1 References

[1] Directive 2000/60/EC of the European Parlament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy (2000).

[2] Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council (2008).

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2 Disk-based solid-phase extraction in water analysis of organic substances

2.1 Abstract

Solid phase extraction (SPE) disks are used in many application fields as modified version of the widespread SPE cartridges. This overview focuses on the application of SPE disks with a standard diameter of about 5 cm for the analysis of organic substances in water. In detail the design and characteristics of SPE disks are regarded as well as various aspects of their application such as the extraction, drying and desorption process and the used analytical method combined with SPE disk based sample preparation. Special applications of SPE disks as passive samplers, as possibility for analyte storage or the reuse of SPE disks are also considered, as well as the possibility of automation of SPE disk procedures.

2.2 Introduction

In the mid-1970s, the solid phase extraction (SPE) technique was introduced [1-3] and was commonly used since 1985 [2]. In 1989, particle loaded membranes named extraction disks were brought on the market by 3M as an alternative to SPE particle-filled cartridges for the handling of large volumes of environmental samples and as solution for many drawbacks of SPE cartridges (see below) [4]. The first paper about SPE disk use was published in 1990 by Hagen et al. for the analysis of environmental pollutants from aqueous matrices [5, 6]. Since 1994, in addition to C_{18} phases other materials such as styrene divinylbenzene (DVB), cation and anion exchange materials were used for disk SPE [7].

In literature, different names and spellings are used for SPE disk such as solid phase extraction disk/disc (e.g. [8]/[9]), extraction disks/discs (e.g.: [10]/[9]), membrane disk (e.g. [11]), SPE membrane (e.g. [12]), membrane extraction disk/disc (e.g. [13]/[14]), particle-loaded membrane (e.g. [15]) or membrane disk SPE (e.g. [16]). “Membrane” in some names originates from the first construction principle of the particle loaded membrane. In this overview, the term SPE disk covers all variants.

SPE disk procedure resembles the handling of SPE cartridges in water analysis (Figure 2.1) [17]. In both approaches, the solid phase material is activated by organic solvents and water to increase the effective surface area and to reduce interferences [10, 17]. Subsequently, the analytes are extracted from the water sample by passing a known sample volume over the phase

material [17]. The analytes are sorbed on the solid phase due to the released Gibbs free energy, consisting of cavity energy and interaction energy contributions from van der Waals and H-bond interactions [18-20]. Also, electronic interactions and ion-exchange processes may be relevant depending on the nature of analyte and sorbent [18]. After drying the sorbents and possibly a removal of interferences the analytes are desorbed from the phase material by small volumes of organic solvents. Thereby the interactions between the analytes and the solid phase material are disrupted [10, 17]. Eventually following a further clean-up and concentration of the organic extract, the extract is analysed [6].

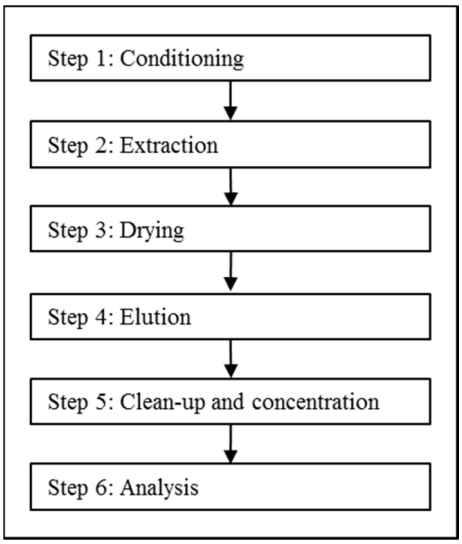

Figure 2.1: Overview of steps in SPE procedures

Since 1978, the SPE technique is commercially available and today, many manufacturers and suppliers offer SPE cartridges and disks with different phase materials and diameters [1]. In literature, documented SPE disk diameters vary from 4 to 96 mm [1, 4]. The dimension of SPE disks normally increases with the sample volume. Therefore, smaller disks are used for small sample volumes, as occur for example in biological and clinical applications [5]. The most frequently used standard SPE disks in water analysis have diameters of 47 mm and are normally used for sample volumes of 0.5 to 1 L [1]. For sample volumes from 5 to 20 L [3] as well as samples containing higher amounts of suspended particulate matter (SPM), SPE disks with diameters between 47 and 90 mm have been used. SPE disks with diameters of 4.6 mm were used in on-line SPE [1, 17].

The most commonly used SPE sorbent is C_{18} modified silica, mainly used for the extraction of non-polar compounds [2, 21]. For the extraction of polar substances such as phenols, DVB is more suitable [21]. It is the most commonly used polymeric resin [2]. Application examples of different sorbents in disk SPE for water analysis are given in Table 2.1. Due to the great variety of available sorbents, selective extraction of substances is possible [21] and thus SPE disks have many fields of application in various analytical areas of interest [5]. SPE disks are widely used in the water analysis for chemicals substances [22]. Nevertheless, to the best of our knowledge there are no previous reviews in water analysis primarily dealing with SPE disks. If SPE disks are mentioned in reviews, the topic is only superficially covered, regardless of the review focus on (I) technical aspects or on (II) substance groups (Chapter 7.2, Table 7.1). Only Thurman et al. regarded in a detailed "introduction" and "general consideration" part different SPE disk formats including construction principles of various SPE disk designs and their practical use [23]. Consequently, this is the first overview focussing on disk SPE of organic substances in water analysis by using standard SPE disks considering different technical aspects.

Table 2.1: Examples for sorbents used in disk SPE for the analysis of organic substances in water, without considering the different disk types

Sorbent	Extracted substances
C_8	Pesticides [24], triazine [14]
C_{18}	Pesticides [8, 25], triazine [14], organochlorine pesticides (OCPs), organophosphorus pesticides, herbicides, insecticides, polychlorinated biphenyls, phthalate esters, polycyclic aromatic hydrocarbons (PAHs) [26]
Graphitized carbon black	Pesticides [27, 28], triazine [14]
Single-walled carbon nanotubes	Nonpolar and polar analytes [29]
Styrene divinylbenzene (DVB)	Pesticides [8, 25], PAHs [30], phenols [21, 31], phenylureas, organophospohorous compounds, triazines [25], Non-ionic aliphatic polyethoxylated surfactants [32]
Sulfonated resin-loaded	Polar organic compounds such as phenols, alcohols, nitro-compounds, aldehydes, esters and haloalkanes [31]
Strong cation exchange (SCX)	Polar pesticides [33]
Strong anion exchange (SAX)	Polar pesticides [33], anionic pesticides [7], organophosphorus pesticides [34], haloacetic acids [35], alkylphosphonic acids [36]

2.3 Characteristics and designs of SPE disks

2.3.1 Characteristics

All characteristics of SPE disks such as high flow rates and reduced risk of plugging are due to the high diameter compared to the thickness [37] independent of the SPE disk designs.

This property reduces the back pressure and leads to steady and high flow rates up to 200 mL/min, compared to SPE cartridges with typically 5 to 10 mL/min [17, 31, 37-41]. A doubling of disk radius leads to an increase of the flow rate by a factor of four [5]. Moreover, the high flow rates and the lower bed volume facilitate the drying of SPE disks compared to SPE cartridges [42].

In addition to the high flow rates, the high cross sectional area of SPE disks reduces the chance of plugging [4, 29, 43] by SPM contained in water samples [44, 45]. Therefore, SPE disks are more suitable for investigation of the whole water sample, i.e., the water sample including SPM, compared to SPE cartridges [46], because samples can be extracted without prior filtration and hence a further sample preparation step can be eliminated [45]. Combined with the high flow rates of SPE disks [47], the extraction is between 1.6 and 6 times faster for disk SPE than for cartridges SPE [4, 5, 48-51] and the analysis time can be decreased [4, 42]. Consequently, SPE disks are more suited for the extraction of large aqueous sample volumes containing SPM [17], which allows the improvement of limits of detection (LODs) [22]. Nevertheless, in literature hardly any study reported on the extraction of large water volumes by disk SPE (Chapter 7.2, Table 7.2), although most authors support the general suitability of disk SPE for the extraction of large sample volumes [38].

Compared to SPE cartridges, the mass transfer characteristics could be improved for SPE disks and therefore the trapping efficiency for analytes at higher flow rates [1, 17] due to the small size of the embedded sorbent particles in the SPE disks [27, 52] (SPE disk: 8-10 µm vs. SPE cartridges: 40-60 µm [4, 17, 31]). The smaller particles improve the uniform packing of sorbents, whereby the mean free path of analytes to the sorbents is reduced and the linear velocity of analytes increase [4, 6]. The high extraction efficiency is linked to high concentration factors and low limits of detection [25, 42]. The fluctuation of adsorption capacity noted by single authors [53] do not agree with our experiences. By the use of an internal standard fluctuation of adsorption capacity can be compensated easily.

Furthermore, channelling is less critical by the use of SPE disks compared to SPE cartridges [27, 54]. This is also due to the compact and uniformly packed, immobilized and small sorbent particles and their high surface area, which are also reasons for the fast sorption kinetics [4, 27,

40]. The occurrence of breakthrough losses caused by channelling [37] is due to insufficient analyte retention or exceeded sorbent capacity [1, 17]. The breakthrough volume, defined as maximum sample volume, which can be extracted with an analyte recovery of 100 % [17], is one of the most important sorbent characteristics [1]. An overview of the theory [2, 17] and a practical example for the calculation of the breakthrough volume by solvation parameter model for DVB SPE disk [55] were already given elsewhere.

The information on the solvent consumption of SPE disk procedures is diverse. It has been reported that solvent consumption can be four to six times higher [47] as well as can be reduced by up to 20 % [1] by the use of SPE disks compared to SPE cartridges. The decreased solvent consumption was attributed to adsorption and desorption phenomena in cartridges, which do not appear in disks due to the large diameter and depending on the amount of sorbent [1]. An argument for high solvent volumes was the dead volume of the used equipment [56]. In essence, the solvent consumption depends on the used setup and the used method and has to be validated.

Beside the comparison with cartridge SPE, disk SPE is often compared with liquid-liquid extraction (LLE). In contrast to LLE, SPE generally requires 90 % to 98 % less organic solvent and the toxicological risk for the workers and costs can be reduced by the reduction of the high purity organic solvents [1, 52, 57-59]. Further advantages of SPE compared to LLE are the avoidance of possible formation of emulsions and foaming [48, 60, 61] and the saving of work, time and money [1, 5, 52]. Additionally, SPE is more efficient [62], enables the extraction of polar analytes [1, 63] and has mostly higher recoveries than LLE [11, 39]. In contrast to LLE, which is classically operated manually [60], SPE is easier to automated [4, 17]. Without doubt, the disk SPE offers many advantages compared to the classical sample preparation methods in water analysis.

2.3.2 Designs

Since the introduction of the SPE disk in 1989 [10, 29, 37, 56], different designs of SPE disks have been developed. In principal, two design principles can be distinguished: (I) substrate immobilised in a web of microfibrils and (II) loose sorbent between two frits in a casing [18]. An overview of the classification and the properties of SPE disks is given in Table 2.2.

Table 2.2: Classification and overview of the properties of SPE disks with a diameter of ca. 5 cm

	Membrane extraction disk				Bakerbond Speedisk	
Sorbent	Immobilized in a web of PTFE fibres [2]		Immobilized in a web of glass fibres [2]		Loose sorbent [18]	
Trade name(s)	Empore SPE disk		ENVI, SPEC SPE disk		Bakerbond Speedisk	
SPE disk diameter(s)	25-90 mm [5, 15, 31, 59]		47-90 mm		50 mm [51, 64, 65]	
Disk holder	Yes		Yes		No	
Max. extraction flow	100 mL/min [38]		-		200 mL/min [38, 39]	
	C_{18}	DVB	C_{18} (1)	DVB	C_{18}	DVB
Thickness	0.5 mm [5]	0.5 mm [15]	1.0 mm [66]	-	1.0 mm [51]	0.5 mm [51]
Weight of sorbent	500 mg [5]	500 mg [15]	-	-	750 mg [51, 64]	300 mg [51]
Total weight of sorbent	570 mg [5]	-	-	-	-	-
Particle						
Shape	Irregular, spherical [5]	-	-	-	Irregular [65]	-
Particle diameter	Ca. 8-10 µm [5]	8 µm [15]	30 µm [66]	-	10 µm [65]	-
Pore size	60 Å [5]	80 Å [15]	70 Å [66]	-	60 Å [65]	-
Surface	-	350 m²/g [15]	-	-	700-1200 m²/g [51]	700-1200 m²/g [51]

-: No information, (1) for SPEC SPE disk, PTFE: polytetrafluoroethylene, DVB: styrene divinylbenzene

(I) Membrane extraction disks

SPE disks in which the sorbent is immobilised in a web of microfibrils of (a) polytetrafluoroethylene (PTFE) or (b) glass are often called membrane extraction disks or SPE membranes and can be differentiated by the material used for the web [37].

(a) The first available PTFE based SPE disk was the Empore disk by 3M [5, 37, 67]. In 1997, the particle loaded membrane disks have started to attract attention [68] and only three years later it was reported that the Empore disks were the most used SPE disks [2]. Until today, Empore disks are the most frequently mentioned SPE disks in literature (Chapter 7.2, Table 7.2). The sorbents of the flexible Empore disks are uniformly embedded in a network of PTFE fibrils with a mass fraction of 90 % [5, 18, 37, 67]. This equals to 500 mg sorbent in a C_{18} Empore disk, with a diameter of 47 mm and a total weight of ca. 570 mg [5, 69]. Less than 1 % of the total surface is PTFE [5]. The packing density is ca. 575 mg/cm³ and similar to density of SPE cartridges and liquid chromatography (LC) columns (600-800 mg/cm³) [5, 15]. An overview on the properties is shown in Table 2.2. Further information is presented in literature on C_8 and C_{18} particles embedded in Empore disks [5, 70] and more detailed kinetic and thermodynamic properties of C_{18} membrane extraction disks [71].

DVB Empore disks are comparable with C_{18} Empore disks (Table 2.2). Only the pore size of the particles is 20 Å larger and is 80 Å for DVB Empore disks. In addition to the mentioned phase materials, (1) silica based sorbents with C_8, SCX and SAX [6, 7, 37], (2) DVB based ion-exchange media for cationic (sulfonic acid) [15, 37, 72] and anionic exchange (tetraalkylammonium) [10, 15, 36, 37], (3) dicarboxylic acid functionality materials for the chelation of metal ions [15], and (4) graphitized carbon sorbents [27] are available.

(b) Glass fiber based SPE disks are available by the trade names ENVI disk or SPEC disk SPE. [66, 73]. Here, the sorbent is embedded in a glass fibre-supporting matrix [1, 2, 17, 37], which is thicker and more rigid and hence enables higher flow rates than PTFE based membrane extraction disks [1, 17]. The particle size as well as the mean thickness of SPEC C_{18} SPE disks is higher than of a C_{18} Empore disks (Table 2.2).

In the market also other membrane extraction disk types exist which are hardly mentioned yet in literature. One example is Atlantic SPE disk (sorbent: C_{18}) for which only one application has been described [74]. Another type is the Resprep SPE disk from Restek, for example available with C_8, C_{18} and DVB sorbents.

For membrane extraction disks an additional SPE disk holder is necessary to extract the water sample by SPE. Normally, ordinary filtration apparatus or similar constructions are used [5, 68, 75]. A more elaborate SPE disk apparatus for Empore SPE disks is shown in Figure 2.2. There, the disk is fixed between the sample reservoir and glass frits by a connector [6]. Similar special SPE disk holders, which are commercially available, are also shown elsewhere (e.g. [73, 76]).

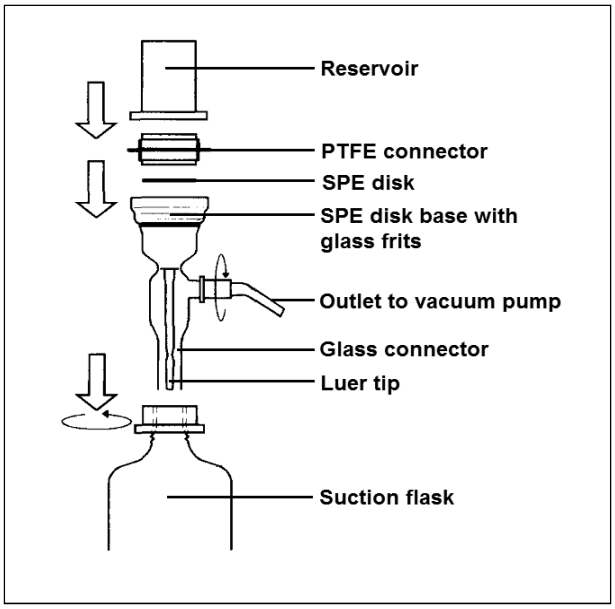

Figure 2.2: SPE disk holder for Empore SPE membrane extraction disk (adapted from [6])

PTFE based SPE disks are often assisted by a support disk because of their flexibility [4, 41, 68, 73]. Glass fiber based disks are more rigid and only for large disks a supporting structure is used [4]. Mostly the supporting structure of the disk holder, as existent in ordinary filtration apparatus, is sufficient. More attention should be paid to the tightness of the setup, which normally fixes the SPE disk between two units (Figure 2.2). Loss of sample or solvent during the elution induces lower recoveries. The tightness depends on the used SPE disk type and the disk holder. Empore disks, for example, conform better to SPE disk holders due to their flexibility and are consequently better compatible with conventional filter apparatus. The influence of the right choice of SPE disk holders was also demonstrated by a detailed investigation of interferences noticed in the determination of pesticides with SPE disk/LC-DAD method, which were finally attributed to the disk housing and phase material [77].

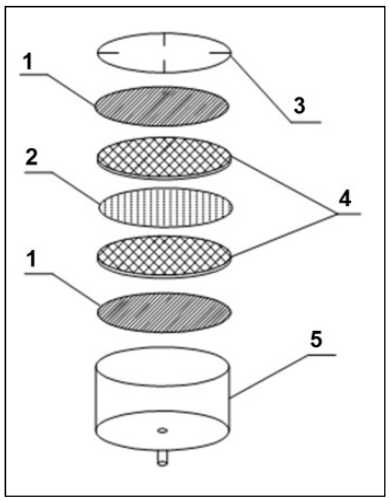

Figure 2.3: Construction of a Bakerbond Speedisk; (1) grid, (2) sorbent, (3) gasket ring, (4) glass fiber filters, (5) casing (adapted from [18])

An alternative to membrane based SPE disks are Bakerbond Speedisks. Here, loose phase material is fixed between two layers of plastic grids and glass fiber filters in a casing, similarly constructed to SPE cartridges (Figure 2.3) [18]. Bakerbond Speedisk is the only SPE disk, which differs from the diameter of 47 mm with a SPE disk diameter of 50 mm (Table 2.2) [38, 51, 64, 65]. The properties of the C_{18} particles used for Empore SPE disks and Bakerbond Speedisks are comparable. However, the C_{18} Bakerbond Speedisk is 50 % thicker than Empore SPE disk since it contains 50 % more sorbent. DVB Bakerbond Speedisk has less than 50 % of the sorbent mass compared with C_{18} Bakerbond Speedisk. The specific surface is the same for both sorbents and higher than for DVB Empore SPE disks. The sorbents are described in detail in the first application of Bakerbond Speedisks [51]. The high flow rates of maximal 200 mL/min due to the other construction principle compare to membrane extraction disks and the filtration membrane on the top of the sorbent (Figure 2.3), in combination with the high capacity enables the extraction of high sample volumes, containing also SPM [39, 51, 78].

In contrast to membrane extraction disks for Bakerbond Speedisks no additional holder is necessary and generally no sample loss is possible caused by the cup-shaped construction of Bakerbond Speedisk (Figure 2.2 and Figure 2.3). They can be directly linked with a vacuum source or vacuum manifold station [51].

Comparison of SPE disk designs

The different disk types all have their advantages and limitations. For extraction of landfill leachate C_{18} Bakerbond Speedisks was preferred compared to C_{18} Empore disk due to quick plugging of C_{18} Empore disk caused by the different construction principles (see above). C_{18} Bakerbond Speedisks allowed a fast and efficient analysis of samples even when samples contained high amounts of SPM, without need of an additional filtration step [38] and saved time because of the higher flow rates compared to Empore disk [1, 18, 38]. Furthermore by the use of Bakerbond Speedisk the occasional occurrence of sorbents in the extract is avoided by a frit in the outlet of the casing (not shown in Figure 2.3).

Beside the above mentioned lower risk of leakage for Empore disks compared to ENVI and SPEC SPE disks by vacuum filtration apparatus, higher recovery for polychlorinated biphenyls (PCBs) were observed for C_{18} Empore SPE disks [73]. In contrast, other authors determined similar recoveries for four organochlorine compounds for SPEC C_{18}, Empore C_{18} and Empore C_8 disks and preferred SPEC C_{18} disk due to higher flow rates, easier handling and cleaner blanks [57]. Similar recoveries were also determined for several PAHs, PCBs, polybrominated diphenyl ethers (PBDEs) and pesticides for four C_{18} based SPE disks and two DVB based SPE disks independent of the manufacturers [79] considering the varied dead volumes of SPE disks at the conditioning of SPE disks and the analyte desorption (see below).

2.4 Solid phase extraction by disk SPE

A high number of SPE disk procedures has been developed for the analysis of organic compounds in different water matrices, such as PAHs, dioxins, PCBs, pesticides, phthalates, organophosphates, phenols, chlorophenols, explosives, semi-volatile organic and organotin compounds and linear alkylbenzenesulfonates [6, 43, 44] and SPE disks were also used in large monitoring projects [80]. An overview of different applications that used SPE disks is given in Chapter 7.2, Table 7.2. Here, only exemplary applications are presented in relation with different technical aspects in the order of the typical steps in SPE (Figure 2.1).

2.4.1 Filtration

Often SPE sample preparation starts with separation of SPM from the aqueous phase prior to the extraction [65] (Chapter 7.2, Table 7.2) due to SPE disks as well as cartridges can be plugged by SPM [5, 19, 39], insoluble inorganic salts of magnesium, aluminium, calcium and iron as well as microorganisms [24, 81]. SPM in natural water is fluctuating between 1 and 1000 mg/L [82-86], influenced by rainfall, surface runoff [87] and hydrological and environmental circumstances [39]. SPM from different sources can have various surface and sorption properties [39]. High contents of SPM can reduce significantly the sample flow rate during the extraction [5, 24]. In particular, for high sample volumes the extraction is then time consuming [5, 19] and the extraction time can increase by a factor of 3 to 15 depending on the type of SPM [88, 89].

Nonpolar compounds such as OCPs and other pesticides with partition coefficients between organic carbon and water ($\log K_{OC}$) > 3 [9] sorb substantially on SPM [39, 77] and organic matter [42] as humic acid, fulvic acids, lipids and proteins [26, 65, 78], respectively, and are influenced by kind of SPM, surface area of SPM and pH value [87]. This can result in a decrease of breakthrough volume and recoveries [78, 90]. Furthermore, a fraction of the analytes remains unconsidered if only the aqueous phase is investigated [9, 39].

By extraction of the whole water sample without prior SPM separation, SPM lies on the top of the SPE disk. Hence, SPM can reduce the flow rate and influence the subsequent drying step depending on the amount of SPM. The remaining amount of water in the SPE disk after finishing the drying process again influences the effectiveness of the analyte desorption process [57, 89, 91]. Detailed information is given in [91]. In any case, the residual water as well as the possible presence of SPM and its different properties should be considered in method development [87, 91-93].

Insoluble inorganic salts of magnesium, aluminium and calcium were tried to dissolve by acidification [24], which can increase the flow rate [5]. However, suppliers do not recommend extreme pH values smaller or equal pH = 2 [24].

The simplest way of SPM separation is filtration [39]. The simplicity and the time saving are reasons, why large monitoring projects and many official standardized SPE methods include a filtration step to avoid plugging and to ensure that only the aqueous phase is analysed [17, 24, 80, 88]. For Empore disks the flow rate can be increased by 75 % by prior filtration without influencing the determination of polar pesticides such as triazines and their degradation products [1, 48, 77]. This explains why filtration is often recommended in association with Empore disks for surface water [1, 9]. The recoveries of phenols at pH = 11 is not influenced by filtration due to the dominance of the anionic species of the analytes in the aqueous phase, which hardly sorb

on SPM and filter material [49]. On the other hand, analyte loss during the filtration step is frequently reported [87], for example for pesticides, using different filter media [42]. Generally, relatively non-polar analytes, such as some pesticides, OCPs, PCBs and PAHs can sorb on SPM and filter materials [39, 48, 65, 73, 77], which was already described in detail [65]. Consequently the analyte concentration is underestimated, if sorb analytes on the filter materials are unconsidered or only the isolated aqueous phase or the SPM is investigated. For analyte determination of analytes sorbed on SPM high amounts of SPM are needed [39]. Therefore, high volumes of water had to be filtrated due to the typically low concentration in natural waters [82-86], linked with the risk of contamination by the filter materials [39].

Plugging already occurs at SPM contents of less than 0.1 % (w/w). The influence of humic acids on pesticide recovery is statistically relevant above 5 mg/L and confirmed that substances with nitrogen groups and basic structures interact stronger with humic acids [94]. Humic acids can only partly be separated by filtration [87] and partly sorbed on the phase material, so that analytes interacting with humic acids were also partly captured [94].

The separation of SPM by filtration was realized by a separated filtration step as well as in-line with the extraction in on-line and off-line modes [4, 68]. For filtration different filter media were used (Chapter 7.2, Table 7.2) such as glass fibre, teflon, nylon, PTFE filters [65] and cellulose filters [38, 65], glass wool, sand and filter aid [38]. Filter aid was mandatory if low recoveries were observed by prefiltration of samples [59, 95]. Empore filter Aid 400 consists of high-density glass beads, prevents plugging [39] and supports the filtration and extraction step of water samples containing high amounts of SPM in on-line and off-line mode [9, 43, 95]. Empore filter Aid is arranged prior to the SPE disk, so that SPM is separated during the extraction step and the analytes can be desorbed from SPM and sorbents in one process step [9, 95] as well as at setup without filter Aid [39, 45, 59]. Due to the reduced number of steps compared to a separate analysis of the phases and enhanced flow, this approach saves time.

Empore filter Aid as well as other filtration media were combined with each other (e.g. [38, 59, 65] and Chapter 7.2, Table 7.2). For example, the combination of Empore filter Aid and MFS GA55 glass fiber filter allows the extraction of more than twice the sample volume until the Empore SPE disk is plugged [43]. Many SPE disk procedures were designed for water samples without SPM [22, 24, 96-99]. As mentioned above, a prior filtration step is not absolutely necessary when SPE disks are used [90]. The water sample including high amounts of SPM can be extracted in a single procedure as well as the analyte desorption from SPE disk and SPM [39, 90]. Consequently, the whole water sample can be extracted by disk SPE, considering the kind and maximal possible amount of SPM [79] and time and work can be saved. In an overview of

the analytical problems during measurements of the total analyte concentration in the whole water sample considering the Water Framework Directive (WFD) [100, 101], SPE disks are even expressly proposed as potential sample preparation method for the whole water sample [39]. SPE disk methods were already successfully developed for the whole water sample by the use of Bakerbond Speedisks [38, 65, 78, 93] as well as other SPE disk types [32, 45, 52, 78, 89, 102, 103].

2.4.2 Extraction

Prior to the extraction of the water sample, the SPE disk is conditioned by organic solvents and water (Figure 2.1) to activate the sorbents [10, 17] and to eliminate impurities from the manufacturing process and the storage [5]. It is recommended to not allow the SPE disk to get dry from the first conditioning step until the extraction is finished [5, 8, 25, 41]. For the conditioning it is advisable to use the same solvents as for the desorption process to prevent extraction of impurities by a solvent exchange. Furthermore, it is reasonable to select solvent volumes which correspond in minimum to the dead volume of the setup to clean the whole setup from possible interferences.

The extracted sample volume varied from 0.02 L [32] to 20 L [3]. In a single case up to 40 L water were enriched (SPE disk diameter: 90 mm) to improve the LOD [104]. However, by increasing the sample volume also the co-extraction of interfering substances increases and the theoretical improvement cannot be achieved [51]. Mostly the sample volume is 1 L and extensive experiences with high sample volumes are missing despite the claim for suitability of SPE disks for the extraction of large sample volumes (Chapter 7.2, Table 7.2) [17].

The flow rate influences the linear velocity and is an important factor for the extraction effectiveness in parallel to the packing density [44]. Low flow rates result in high extraction recoveries [105]. Whether positive or negative pressure is used to transport the sample over the SPE disk does not influence the extraction efficiency [43]. Generally, the flow rate varies between 1.5 [61] and 200 mL/min [51, 64, 106] and is mostly about 50 mL/min (Chapter 7.2, Table 7.2).

A well-known approach recommended by the suppliers is the addition of low volumes of an organic solvent (e.g. methanol, ethanol), also called modifier [8, 9], to the water sample as wetting agent for the sorbent [24, 31, 42] and to stabilize [4] and increase the extraction flow rate up to 30 % [43]. Moreover, the organic modifier should prevent analyte adsorption on the container [30, 62, 65], for example of pesticides on teflon or glass containers [65]. To prevent

sorption of PAHs different modifiers and concentrations up to 30 % were investigated [30, 62]. The best results for PAHs were obtained at 15 % (v/v) acetonitrile or 20 % (v/v) 2-propanol depending on the molecular weight of the investigated PAHs and the high solvent volumes significantly influenced the LC-fluorescence detection (FD) method due to impurities of the used solvents [30]. Organic modifiers were also used for improvement of the extraction of more polar compounds such as phenolic compounds [11] and organophosphorous insecticides [69]. The regularly used volume of organic modifier is small, so that the modifier does not negatively influence the extraction efficiency and subsequent analytic and investigations on the influence of organic modifiers on the extraction efficiency were not required. The volume of organic solvent is for example 5 mL per litre sample (0.5 % (v/v); e.g. [9, 31]) and only in exceptions 25 mL (2.5 % (v/v)) or up to 300 mL (30 % (v/v)) solvent per litre sample were added [24, 30]. Although high fractions of organic modifier can decrease the extraction efficiency, no systematic study on the influence of organic modifier on the extraction efficiency of polar compounds is known to us. Furthermore, a modifier is not absolutely necessary and mostly no modifier is used (Chapter 7.2, Table 7.2).

The influence of pH value on the extraction efficiency depends on the analyte properties and was investigated by different authors (pH = 2 to 10 [22], pH = 3 to 12 [95]), who showed that the highest recoveries were determined under acidic conditions for the investigated pesticides [22, 95]. Due to the negligible degree of protonation the extraction efficiency is nearly pH independent for crown ether (pH = 3 to 7) [44] as well as for diazinon [107]. Similar results are also described in literature for phenoxy acid herbicides [108].

The analyte retention can be influenced by addition of salt, called salting-out effect. For example, for organophosphorous compounds and herbicides, 10 to 100 g/L sodium chloride were added to increase the retention [9, 25]. Other users added 1 [41] to 10 % (w/v) [109] sodium chloride or up to 20 % (w/w) [26, 49]. In practice, natural water already includes different salt contents [95, 105] which makes exact salt adjustment difficult and not always necessary [105]. Moreover, the addition of salt to the sample takes time. So far, only few studies dealing with the salting-out effect in combination with disk SPE [9, 26, 41, 49, 94-96, 105, 109] and in particular, the influence of salting-out on polar substances is not completely understood. In the literature, contradicting statements are found [9, 110] and further investigations are required.

Immediately after the extraction step, it is reasonable to rinse the equipment, which had contact with the sample, to reach the best possible recoveries. Normally, blank water is used for rinsing the equipment to transport remains of the aqueous sample and SPM from the sample bottle to the SPE disk completely.

2.4.3 Drying

Traces of residual water between 0.1 and 1.0 mL after the extraction of analytes from the water sample [76] can influence the choice of organic solvents [58, 61, 81, 89, 111, 112], the elution strength and the subsequent solvent exchange as well as a derivatization and instrumental analysis [58, 113-115]. To prevent analytical problems and to achieve high recoveries and reproducible results the volume of water should be as small as possible or be precisely defined [76, 111, 116]. Therefore, in many SPE disk procedures the residual water is removed by a drying step [80]. So far, very few studies are dealing with this topic [61, 115, 117, 118] and many questions are still open, for example which factors influence the effectiveness of the drying process by the use of vacuum. A first approach shows a dependency on a numbers of factors such as the sorbent, the fixation and the amount of sorbent, the pumping settings, the duration of the drying process and SPM content in the sample [91]. Nevertheless, a direct transfer of the results on different systems is not possible until now.

The most frequently used and easiest way to dry a SPE disk is to apply vacuum or in exceptions to lead a gas stream over the SPE disk [107, 119] analogously to the extraction step [17]. The drying times vary between 0.5 min [26] and 45 min [42, 68]. About 75 % of the applications have drying times shorter than 10 min (Chapter 7.2, Table 7.2). Due to the absence of general information on the drying process, an optimum drying time has to be determined during the method optimization.

In addition to the drying by vacuum, residual water in the extract is often removed by a drying agent. Therefore, the eluate is filtered over the agent, normally anhydrous sodium sulfate (e.g. [26, 65, 75] or Chapter 7.2, Table 7.2). The method was also successfully used for on-line applications [97, 102, 120-122]. The comparison of effectiveness of different drying agents resulted in copper sulfate and silica as the best drying agents in on-line disk SPE and could be used up to 100 times. Molecular sieve and calcium sulfate were less suitable and plugged the gas chromatography (GC) column [115].

DryDisks are an alternative to powdery drying agents and were used as such. DryDisks are membranes that separated organic solvent from an aqueous solution [123] and were also used in

combination with sodium sulfate since sodium sulfate alone was not sufficient [97]. Also other drying types were successfully combined, for example 15 min vacuum drying with 10 min at 100 °C [36]. To find most suitable storage conditions up to 30 day, four desiccation methods of SPE disk in pesticide analysis were compared. The comparison showed that differences were small among the tested combinations of drying agents, vacuum, storage period and temperatures, whereby 24 h freeze-drying was the fastest method for the removal of residual water [117]. Although all named methods are successful, the combination of different drying methods is labour-intensive and the steps are difficult to automate. Whereas, SPE disk drying by vacuum is an effective drying method, save work and is easy to automate, compared to the mentioned alternative methods. Nevertheless, further investigations are required for a more detailed understanding of the influencing parameters.

2.4.4 Desorption and analysis

The analyte desorption from the SPE disk can be performed in different ways and is directly connected to the used analytical method. In principle, three approaches can be distinguished: (Ia) elution of the SPE disk and subsequent analysis of the extract, (Ib) suspending the SPE disk in a solvent followed by investigation of the solvent and (II) direct detection of analytes on the SPE disk without desorption step, e.g., by solid state spectroscopic techniques [2].

(Ia) Elution is by far the most used desorption process in connection with SPE disks (ca. 80 %; Chapter 7.2, Table 7.2). As mentioned above, small volumes of suitable organic solvents pass through the disk [1, 2, 5]. The eluent polarity [95] and volume are important for the extraction efficiency [16, 22]. Analogous to the conditioning of the sorbent, the minimum solvent volume should correspond to the dead volume of the setup to collect all sorbed analytes. For a complete desorption of all analytes, it is better to use the double or triple of the dead volume for the elution step. The dead volume of the isolated SPE disk can significantly differ and perhaps change, if different SPE disks are tested during the method development. For example, the dead volume of an isolated C_{18} SPEC is ca. five times smaller than for the isolated C_{18} Bakerbond Speedisk, with a dead volume of about 4.0 mL.

For desorption different solvents were used such as acetone [93], acetonitrile [25], ethyl acetate [49], dichloromethane [26] or methanol [48]. To achieve high recoveries, also mixtures of different solvents (e.g. [8, 95]) and sequential combinations of solvents (e.g. [65]) have been used for the elution step. Regularly the desorption solvent is given in aliquots on the SPE disk (e.g. [5, 8, 48, 49]) and although SPE disks allow fast flow rates, the elution should be done

slowly to enable sorbent wetting by the solvent [24]. For the same reason, the vacuum is stopped for few minutes during the elution to allow the elution solvent to soak in the SPE disk. A special kind is the back-flush elution used in on-line methods [28, 95, 109], where the elution is carried out in the opposite direction to the flow during enrichment. Regularly, the extract is concentrated before it is analysed [5] (Chapter 7.2, Table 7.2).

(Ib) In another desorption type, the analytes are transferred from the SPE disk to the liquid phase, however not by elution, and are then analysed in the liquid phase. This can be implemented for example by supercritical fluid extraction (SFE) [61, 81, 89, 105]. A short overview on SPE disks coupled with SFE was already given [124] and this combination was also mentioned in other reviews [1, 13]. The similar accelerated solvent extraction (ASE) was used for analyte desorption from SPE disks [32, 125]. In addition, microwave extraction for the desorption of pesticides [126], phenolic compounds [11] and other organic compounds [26] was applied. In single cases, the SPE disk was placed into a vial covered by solvent and finally the solvent was analysed (in-vial desorption) [63, 127]. Sometimes the vial was heated up to ca. 100 °C or the solvent filled vial with SPE disk was additionally shaken [128] to enhance desorption [36, 129]. Ultrasonic supported [33, 80] and Soxhlet extraction [104] was also performed for SPE disks. Normally, all mentioned methods are as efficient as elution and can be replaced by elution, which is mostly less labour-intensive and time-consuming than these methods. With one exception [63], a direct comparison of various desorption methods in disk SPE is not known to us and this exception showed higher recoveries for the elution compared to in-vial desorption [63].

Independent of the desorption method after eventual further treatment, for example by concentration or solvent exchange to increase the sensitivity the received extracts are investigated by an analytical method (Chapter 7.2, Table 7.2). The choice of the analytical method depends on the analyte properties, the analyte concentration and the solvent. Normally, the analytes are separated by GC or LC prior to their detection, whereby GC is regularly coupled with mass spectrometry (MS) and LC with ultraviolet-visible (UV-VIS) spectroscopy or MS (Chapter 7.2, Table 7.2). Furthermore, disk SPE was coupled with several other analytical methods such as micellar electrokinetic chromatography (MEKC) [96], TLC [126] or different toxicity tests (e.g. D. magna test or elongation test [88]). The description of these analytical methods is out of the scope of this review.

(II) Sorbed analytes are also analysed directly on the SPE disk. For example, the analytes can be desorbed directly from the SPE disk by laser desorption followed by fourier transform mass spectrometery (FT-MS) analysis [130] or, after adding a matrix solution, the analytes are

detected by matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) [131]. To overcome problems with MALDI, surface-assisted laser desorption/ionization (SALDI) was used by changing the laser intensity [27]. PAHs were detected directly on SPE disks by fluorimetric detection [53, 132] or by room-temperature phosphorimetry [66]. Quantification was only feasible by the use of SALDI, fluorimetric detection and room-temperature phosphorimetry. The direct detection of analytes on SPE disks is hardly applied, up to now. The approach of direct analysis of analytes on SPE disks is maybe of future interest to save time and material due to the elimination of the separate desorption and analysis process if no analyte separation is necessary.

2.5 Special applications of SPE disks

2.5.1 Passive sampler

SPE disks are also used as passive samplers [133]. To that end, after conditioning [133], the SPE disk is exposed to a liquid sample during a defined time period [2], e.g. as time integrative passive sampler for polar organic contaminants in water, and accumulates analytes on the SPE disk [33, 134]. For repeatable recoveries, it is important to minimize the occurrence of bubbles and turbulences during extraction by positioning of the passive sampler horizontally to the surface of the flowing water [33, 135]. Analogously to standard disk SPE procedures, the SPE disk is subsequently dried [2, 133] and the analytes are directly analysed after extraction [2]. The general acceptance of passive samplers for organic compounds is still rather small, caused by difficulties in their calibration [134]. Due to different sorption mechanisms, the calibration of performance reference compounds is not uniform [134]. Alternatively, kinetic studies with and without deuterated compounds were performed in the laboratory by the use of C_{18} [135], DVB-XC [33], DVB-RPS Empore [33, 134] and polydimethylsiloxane (PMDS) disks [134] and flow systems. Also the influences of the construction of passive samplers, including different membranes for the protection of SPE disks against biofouling, on the uptake kinetics were tested by the use of a flow system at constant test conditions [133]. Until now, no satisfactory solution for the calibration of passive samplers under real conditions was found due to the dependency of the kinetic constant on numerous factors, for example temperature, pH value and turbulences on sampling rate [33, 135] and further investigations are required.

2.5.2 Storage of analytes on SPE disks

Several studies investigated the stability of analytes on SPE disks during different storing conditions, to simplify the storage and transport of the samples over long distances and time periods by replacing the sample bottles against the SPE disk to save space, weight and money and avoid broken glassware [36, 42, 52, 136].

In different studies, it was found that pesticides can be stored safely on SPE disks [24, 90]. Some studies indicated that pesticides have a higher stability on SPE disks than stored in water [42, 76, 117, 136] due to the protection of analytes on the SPE disk from microbiological degradation, sorption on SPM and hydrolysis [90, 136]. Nevertheless, hydrolysis can occur caused by residual water in the SPE disk after water sample extraction. Therefore different drying methods were investigated [117] (see above).

Also the stability of analytes at different storage times and temperatures was tested. No degradation of endosulfan [80, 137] and other pesticides [136] and of 23 PAHs [76] at temperatures smaller or equal +4 °C was observed within three [80, 137], six [136] and two [76] months. A loss was determined up to 10 % at +4 °C and up to 24 % at room temperature for pesticides, within three months, depending on water matrix, storage temperature and analyte properties as for example vapour pressure and solubility [138]. The best storing conditions for time periods up to six month were found at -20 °C [136, 138].

Following this, the transport and storage of analytes on SPE disks are in principle possible and has many advantages for simplification of the procedure [36, 52, 76]. Since information is scarce until now, the possibility of storing and transport should be checked in every case of matrix and analyte change, especially for the whole water sample. So far, no study on the optimal storage conditions for the whole water samples is known.

2.5.3 Reuse of SPE disks

A few studies reported about the reuse of SPE disks. For the analysis of pyrethroids in deionized water by SPE/GC-ECD, no significant differences on the recovery by reusing C_{18} SPE disks were found [42]. In another case, ten stacked SPE disks (SPE disk diameter: 4.6 mm) were used for ten analyses of tap water without influence on the performance. However the method could not be recommended for the analysis of river water [120]. Similar results were reported in a feasibility study of EPA Method 632 for diuron. Here, the reuse worked well for drinking water with low background interferences [139].

In general, the reuse of SPE disks seems possible for water samples without high contents of potentially interfering matrix and if no memory effects seem likely.

2.6 Automatization

SPE is a flexible, environmentally friendly and easily automatable sample preparation [10]. One of the main advantages of an automated SPE is the safety due to less personal contact to hazardous samples and chemicals. Additionally, the precision and the accuracy can be improved and monotonous work and time exposure can be reduced by an automated method [140]. Also the chance of contamination and analyte loss during a concentration step by evaporation can be reduced [1, 67]. Furthermore, an automated method development and high sample throughput are in principle possible. Potential limitations are carryover, systematic errors, e.g. incomplete sample transfer, which also affect the precision and accuracy, and physical and chemical sample instabilities. All these points depend on the used automated system. Principally, the automated methods have to be differentiated in (I) off-line and (II) on-line automated SPE methods.

(I) In contrast to an on-line automated method in the off-line automated method the automated SPE system is not linked with the analyser system.

One commercially available automated SPE disk system is the Autotrace. The semiautomated system enables the enrichment of up to six samples on SPE disks or cartridges with a maximum flow rate of 60 mL/min. With Autotrace organochlorine compounds [57], phenyl urea herbicides [121], rotenoids and piperponyl butoxide [102] in water were investigated by the use of Empore [57, 102, 121] and SPEC SPE disks [57]. However, the Autotrace is only partly suitable for water samples containing SPM since the sample is sucked into the apparatus through thin tubes, which could easily lead to blockages by SPM.

Another automated system is the SPE-DEX 4790 extractor of Horizon Technology. Up to eight SPE-DEX 4790 extractors, each for one SPE, can be coupled for SPE disks with diameters of 47 to 90 mm. The sample bottle can be automatically rinsed. In literature effective extractions were described for PAHs [93], pesticides [97] and perfluorinated chemicals by the use of C_{18} Speedisk [93, 97] and Atlantic HLB [74] SPE disk and SPE-DEX 4790 extractor.

(II) In on-line automated methods, one or more small SPE disks (diameter < 47 mm) are stacked in specially designed holders used similar to pre-columns in LC [67, 141]. To prevent peak broadening, it is recommended to use a comparable sorbent as the analytical column, which was implemented by the enrichment of dicamba, 2,4-dichlorophenoxyacetic acid and atrazine on one C_{18} Empore disk (diameter = 8 mm) [142]. In all other here mentioned on-line automated

methods, more than one SPE disk was used to improve the limit of detection [25, 67, 109, 120] or to adapt the sorbents and the capacity on each individual analytical challenge by the use of various sorbents and numbers of SPE disks, which is not possible by classical pre-columns [67, 143]. In on-line automated methods up to ten SPE disks were used [92, 109, 120], whereby in manual methods only up to two SPE disks were combined to increase the capacity [11] or to combine the properties of different phase materials [7, 96, 144, 145]. The drawback by the use of small SPE disks is that the advantages of SPE disks such as the high flow rates and the reduced chance of plugging are not valid anymore. As far as known, no on-line system for SPE disks with diameters of about 5 cm is available and although such a system would be desirable for the extraction of the whole water.

2.7 Conclusions and outlook

The interest in SPE disks has not increased as fast as postulated 15 years ago [6] and cartridge SPE is still the dominating sample preparation method in laboratories for water analysis, complemented by several other sample preparation techniques [93, 146] as for example LLE or solid phase micro extraction (SPME). Although cartridge SPE is 30 to 50 % cheaper than disk SPE [1], already now disk SPE is used in various fields of applications, from classical SPE to passive sampling, and has several advantages such as high flow rates and reduced risk of plugging. These advantages allow disk SPE to meet the requirements of the WFD to cover the whole water sample, to achieve the partly very low LODs [100, 101] and offer the potential to save time, work and money. Consequently, disk SPE is still a promising method in water analysis for the future and is subject to standardization efforts [39]. Disk SPE is a fast, efficient and reproducible sample preparation method, facilitates the transport and the extraction of high sample volumes and enables automatization.

In future, further investigations, for example on the understanding of the drying process in disk SPE, on the storage of whole water sample extracts on SPE disks and on an automated on-line SPE disk system for the whole water sample with standard SPE disks are required and will support the acceptance of SPE disks in water analysis of organic substances.

2.8 References

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3 Occurrence of residual water within disk based solid phase extraction and its effect on GC-MS measurement of organic extracts of environmental samples

Redrafted from "C. Erger, P. Balsaa, F. Werres, T.C. Schmidt, Occurrence of residual water within disk-based solid-phase extraction and its effect on GC-MS measurement of organic extracts of environmental samples, Anal. Bioanal. Chem. 403 (2012) 254", DOI 10.1007/s00216-011-5659-y,

3.1 Abstract

Solid phase extraction (SPE) is a widespread and powerful sample preparation technique in many analytical areas. Many of the used methods reduce residual water during sample preparation by drying the phase material. Despite the importance of this step, hardly any study deals specifically with the drying process, and if so, only few aspects are mentioned. The present study is the first systematic investigation of the drying process using SPE disks, including the influence of process parameters on the amount of residual water and its consequences for subsequent elution and gas chromatography-mass spectrometry (GC-MS) analysis. The following points were investigated in detail: (i) the change of pressure and volume flow during the drying process, (ii) the remaining amount of water at different drying times for different SPE materials, (iii) the influence of suspended particulate matter (SPM) on the drying process and (iv) the effects of the residual water on the elution step by using different organic solvents. The study shows that the volume of residual water in the SPE disk is affected by the fixation of the sorbent, the phase material, the amount of sorbent, the pumping settings and the duration of the drying process. Furthermore, systematic investigations demonstrate the influence of residual water on the GC-MS analysis and show analytical interferences only for a few of the investigated analytes. All results suggest that more problems in SPE/GC-MS methods are caused by residual water than previously assumed.

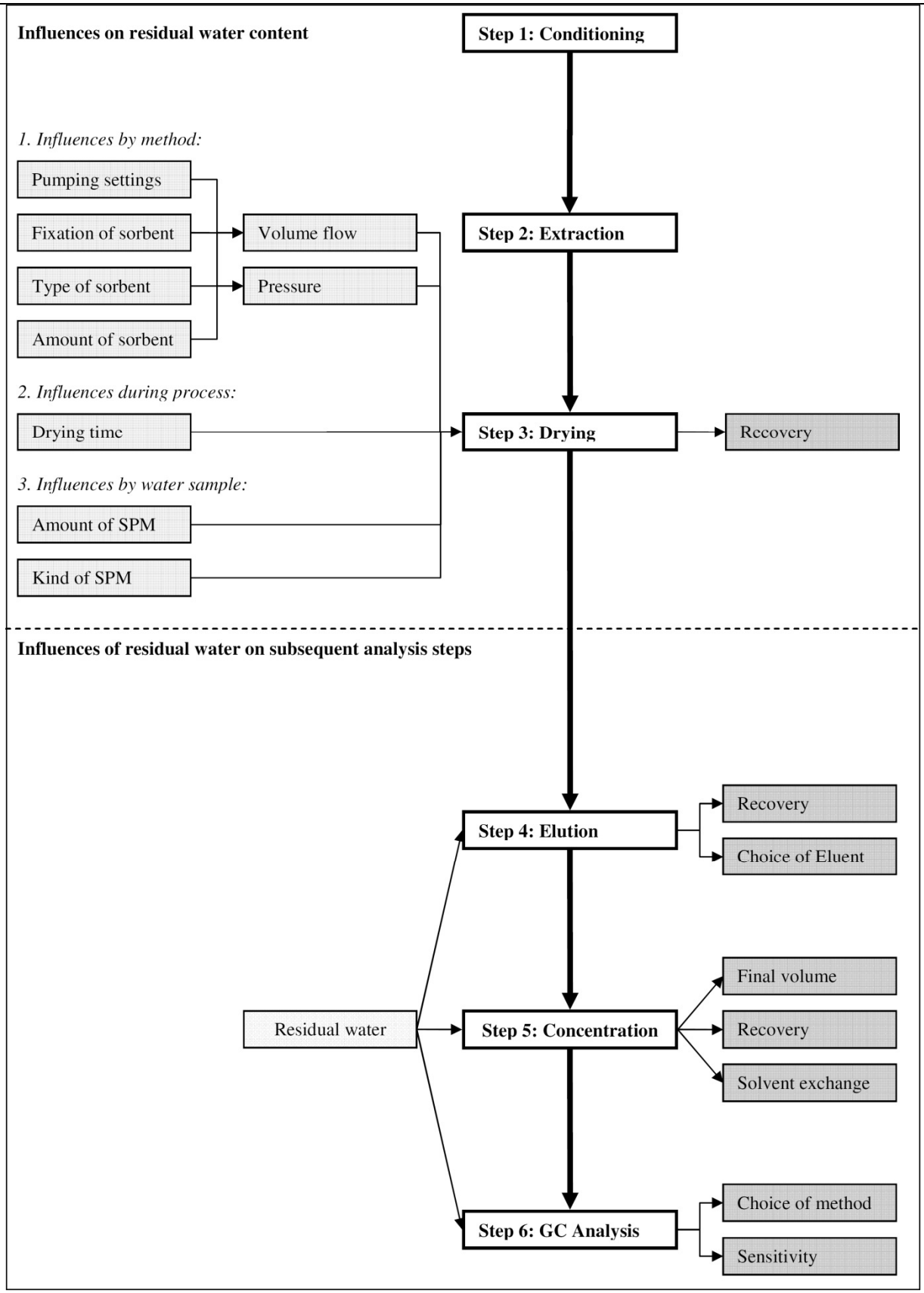

Figure 3.1: Parameters influencing residual water formation and effects of residual water on subsequent steps of SPE procedure and analysis

3.2 Introduction

Solid phase extraction (SPE) is a powerful and therefore widespread sample preparation technique in clinical, biochemical, pharmaceutical and environmental analysis [1-3]. It is used for matrix separation, rapid clean-up and enrichment of target compounds preceding chromatographic analysis [2-5]. The technical principle is based on the distribution of analytes between a solid and a liquid or a headspace vapour. In water analysis, the typical SPE process starts by sorbent cleaning, followed by the activation and the conditioning of the sorbent generally by an organic solvent and water (to remove the excess activation solvent) and the extraction of compounds from the water sample. The subsequent steps are the removal of interferences (clean-up) and water, and finally the elution of sorbed analytes (Figure 3.1) [3,4,6]. Many of the reported methods reduce the remaining water volume on the phase material after the extraction step by actively drying the sorbent [4,5,7-12]. The reasons for this step are manifold [13,14]. Residual water may hamper the elution of sorbed analytes by a non-polar solvent, e.g. n-hexane, and reduce the recovery of the analytes [9,15-18] or can influence the elution strength of solvents by mixing [16]. Furthermore, residual water can disturb the subsequent solvent exchange to another solvent [5]. Reduction of the volume of residual water can also be a prerequisite for a derivatisation step after elution. For silylation, for example, it is necessary to eliminate water as completely as possible [19]. Finally, residual water on the phase material can induce interferences in the instrumental analysis step [4,5,10-12,16,20-22]. Van der Hoff et al. reports that small quantities of water can result in a rapid deterioration of the gas chromatography (GC) system. In the on-column introduction technique, this problem can be alleviated to some extent by using properly deactivated retention gaps [12]. Furthermore, the use of bonded and cross-linked stationary phases can prevent the damage of GC columns by water and organic solvents [23], which makes it even possible to carry out direct aqueous injection in GC analysis with comparable results to other techniques [24].

The points mentioned above demonstrate the importance of the drying process and the potential adverse effects of remaining water [9,12,18,25]. It is well known that the amount of water after the drying step should be as small as possible or be precisely defined to prevent analytical problems and to achieve high recovery and reproducible results [15,25]. Surprisingly, hardly any study deals specifically with this subject, and in the existing ones, only few aspects are covered [6,11,12,18]. Pico et al. studied the use of several drying agents for the effective removal of water traces from the desorption solvent [20]; Zorita et al. checked the effects on polychlorinated biphenyl (PCB) recoveries by drying the SPE disk under vacuum with and without additional

drying in a desiccator [9], and van Hout et al. determined the remaining amount of water in the stationary phase of SPE disks at different drying times [21]. Finally, Senseman and co-workers investigated four desiccation methods for SPE disks after enrichment of pesticides in order to determine whether enhanced stability would result when residual water was removed from the disks before storage. They also added anhydrous sodium sulphate to the eluate to remove any excess water [13].

The study presented here was done in the framework of the method development for a multi residue analysis of 54 non-polar organic compounds in surface water containing suspended particulate matter (SPM) by SPE disks and gas chromatography-mass spectrometry (GC-MS). It quickly became apparent that residual water after the drying step has a big influence on the results of the whole method. Therefore, the first extensive and systematic investigation of the vacuum-based drying of SPE disks was carried out in this study.

3.3 Experimental

3.3.1 Materials

For investigation of the drying process, an SPE disk apparatus by Varian Inc. and a SPE manifold station by J. T. Baker were used.

Bakerbond Speedisk Extraction Disk C_{18} (diameter: 50 mm), Bakerbond Speedisk Extraction Disk H_2O Phobic DVB (diameter: 50 mm) and Bakerbond Speedisk Extraction Disk H_2O Phobic DVB – high capacity (hc) (diameter: 50 mm) are available at J. T. Baker and the Varian SPEC C_{18} SPE-disk (diameter: 47 mm) was received from Varian Inc..

3.3.2 Solvents, chemicals and standards

All organic solvents used for the solutions and experiments were picograde and obtained from LGC Standards GmbH.

Tap water filtered through activated carbon was used as blank water, and nitrogen 5.0 and helium 5.0 were used at the concentration and analysis step.

The certified sediment standard PAH Loamy Clay 1 was purchased at LGC Standards GmbH.

The following standards and stock solutions were available at the Cambridge Isotope Laboratories, Dr. Ehrenstorfer, Fluka, LGC Standards GmbH, National Physical Laboratory (UK), PAH Research Institute, Riedel de Haën, SERVA and Ultra Scientific: alachlor, aldrin, atrazine, chlorfenvinphos, chlorpyrifos-ethyl, dieldrin, p,p'-(dichlorodiphenyl)-2,2-

dichloroethylene (p,p'-DDE), 2,2-bis(o,p-chlorophenyl)-1,1,1-trichloroethane (o,p'-DDT), p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT), p,p'-(dichlorodiphenyl)dichloroethane (p,p'-TDE), endrin, alpha-endosulfan, beta-endosulfan, hexachlorobenzene, hexachlorobutadiene, alpha-hexachlorocyclohexane (alpha-HCH), beta-hexachlorocyclohexane (beta-HCH), gamma-hexachlorocyclohexane (gamma-HCH, lindane), delta-hexachlorocyclohexane (delta-HCH), isodrin, pentachlorobenzene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene and 1,3,5-trichlorobenzene, trifluralin, simazine, polycyclic aromatic hydrocarbon (PAH) - mix by EPA (acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-c,d]pyrene, naphthalene, phenanthrene, pyrene each 100 µg/mL in acetonitrile; LGC Standards GmbH), polychlorinated biphenyl (PCB) Mix 1 (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180 each 10 ng/µL in acetone; Dr. Ehrenstorfer), acenaphthene-D_{10}, anthracene-D_{10}, atrazine-D_5, chrysene-D_{12}, 4,4'-dibromoctafluorobiphenyl, 3,4-dichloronitrobenzene, fluoranthene-D_{10} and 4-n-nonylphenol-D_8. The last eight substances were used as internal standards, whereby fluoranthene-D_{10} was used as volumetric standard. Generally, the analytical standards were used to prepare fortification, standards and spike solutions. All stock solutions were prepared by weighing and dissolving in ethyl acetate or acetone and stored at 4 °C. After spiking, the concentrations of PAHs in the samples were 100 ng/L and of all other analytes 50 ng/L. Concentrations of internal standards in 1 L sample varied from 0.1 to 1.12 µg/L depending on sensitivity.

3.3.3 Determination of the volume flow

The volume flow was determined by a self-made gas flow meter. This consists of a simple glass tube of a volume of 1.2 L. In the glass tube soap bubbles move with different velocities depending on the volume flow during the drying process of the SPE disk. The gas flow meter is in-line with the SPE disk holder and the water jet pump and in the case of vacuum drying arranged also by this order.

For the experiments, the volume flow was determined for the original C_{18} SPE disks and during the drying process. Before determining the volume flow for the latter one, SPE disks were twice conditioned with 4 mL acetone and 4 mL water (contact time: 1 min) and 50 mL tap water was enriched to simulate the enrichment process.

3.3.4 Water residue in SPE disks during the drying process

The water residue in extraction disks was determined for four kinds of SPE disks during the drying process. At the beginning, the extraction disks were conditioned twice with 6 mL acetone and 6 mL water (contact time: 1 min) followed by the enrichment of ca. 1 L tap water or blank water (50 mL/min). Afterwards, the SPE disks were dried by vacuum for max. 60 min. The water residue was determined by weighing the SPE disk during the drying process and subtracting the weight of the original SPE disk.

3.3.5 Influence of the drying time on the effectiveness of the elution step

The Bakerbond Speedisk Extraction Disk C_{18} was conditioned twice with 6 mL acetone and 6 mL water (contact time: 1 min) followed by the enrichment of ca. 1 L of a spiked blank water sample within 30 min. Afterwards, the SPE disk was dried for 7 min or 60 min, respectively. Subsequently, the analytes were extracted three times with 3 mL acetone (contact time: 1 min, 5 min, 1 min). Finally, 100 µL of the volumetric standard (2.1 mg/L) were added to the combined eluates and analysed by GC-MS. Every variation of the drying time was investigated for three samples (n = 3).

3.3.6 Recoveries of different elution solvents (with and without sediment)

The Varian SPEC C_{18} SPE disk was conditioned analogously to the investigation of the influence of the drying time on the effectiveness of the elution step. Afterwards, ca. 1 L blank water spiked with analytes or 500 mg certified sediment was enriched on the SPE disk, followed by drying the extraction disk for 30 min. Then, the analytes were extracted four times with 4 mL of an organic solvent (acetone, ethyl acetate, dichloromethane, n-hexane or tetrahydrofuran; contact time: 5 min, each). After the addition of 100 µL volumetric standard (2.1 mg/L) to the combined eluates, the extract was concentrated to 1.5 mL at 40 °C (water bath) in a gentle stream of nitrogen. Finally, the eluates were analysed by GC-MS. Every elution solvent was investigated twice (n = 2), and additionally a blank sample was investigated. The sediment spiked samples were investigated once (n = 1).

3.3.7 Influence of water on GC-MS analysis

A reference solution of all investigated analytes, internal standards and volumetric standard (1120-100 µg/L) was spiked with 0 % vol., 10 % vol. and 20 % vol. water and analysed by GC-MS.

3.3.8 GC-MS analysis

The eluates and solutions were analysed by a GC 6890/MSD 5973 of Agilent Technologies equipped with a cooled injection system (CIS) 4 by Gerstel GmbH & Co. KG. The analytes were ionised in electron impact ionization mode (EI mode, 70 eV) and detected in selected ion monitoring (SIM). The compounds were identified by their retention times and up to four selected mass to charge ratios (m/z-ratio). One m/z-ratio was used for quantification. Separation was performed by a Zebron ZB5 ms (30 m x 0.25 mm x 0.25 µm) capillary column by Phenomenex Inc.. Helium was used as carrier gas at a constant flow of 1.0 mL/min. After the injection of 1 µL solution to be investigated, the CIS temperature was increased with 12 °C/s from 80 °C (0 min) to 300 °C and hold for 5 min. The injection was carried out in splitless mode by a splitless time of 0.5 min, a purge flow of 10 mL/min and a purge time of 2.00 min (gas: nitrogen). For the GC separation, the oven temperature was increased with 10 °C/min from 50 °C (0 min) to 300 °C and the temperature was held for 5 min. The total runtime amounted to 30 min. The temperature for the transfer line and the ion source were set to 280 °C and 230 °C.

3.4 Results and discussion

3.4.1 Drying

Volume flow

The drying step is an important and significant process step in SPE and follows the extraction of the water sample (Figure 3.1). One important factor influencing the drying process is the volume flow. This was investigated with two setups that differed only in the SPE disk types and therefore in the fixation of the sorbent. The results show that the measured volume flow through the original, non-conditioned Bakerbond Speedisk Extraction Disk C_{18} was 2 L/min less than the volume flow through the Varian SPEC C_{18} SPE disk in spite of applying the same vacuum on the SPE systems. For the Varian SPEC C_{18} SPE disk, a volume flow of 5.8±0.2 L/min (relative standard deviation (RSD) = 4 %, n = 4) was determined leading to a vacuum pressure of -54±10 mbar for the original extraction disk. For the Bakerbond Speedisk Extraction Disk C_{18} a volume flow of 3.8±0.1 L/min (RSD = 3 %, n = 4) was measured leading to a vacuum pressure of -173±10 mbar. These differences were attributed to the SPE disk type and the fixation of the sorbent. In the Varian SPEC C_{18} SPE disk, the C_{18} phase material is bound to silica particles that are woven into fibreglass, and the disk is clamped like a filter in a filter apparatus in the SPE system by Varian Inc. [26,27]. In contrast, loose C_{18} phase material is used for the Bakerbond Speedisk Extraction Disk C_{18}. The SPE disk is constructed similar to a normal SPE cartridge but with a larger diameter [27,28].

Pressure and volume flow also differ for both SPE systems during the drying process of wet extraction disks (Figure 3.2). This is again due to the different SPE disk types and fixation of the sorbent. Furthermore, in spite of application of a constant working vacuum pressure system, the real pressure increases by 100 to 200 mbar and the volume flow increases on average by about 1.3 L/min during the drying process. These observations can be explained by the decreasing amount of water in the sorbents and therefore the decreasing resistance to the gas flow during the drying process. The different change of the volume flow of the SPE disks over time is also caused by the different SPE disk types. Theoretically, the volume flow should be constant, when the extraction disks are dry again. Figure 3.2 shows a nearly constant volume flow for the Varian SPEC C_{18} SPE disk after ca. 10 min drying. Despite being constant, the volume flow of the previously wet SPE disks did not nearly reach the volume flow for both SPE disk types of the original dry extraction disk within 45 min. This suggests that the phase material is irreversibly altered during the steps of conditioning and enrichment.

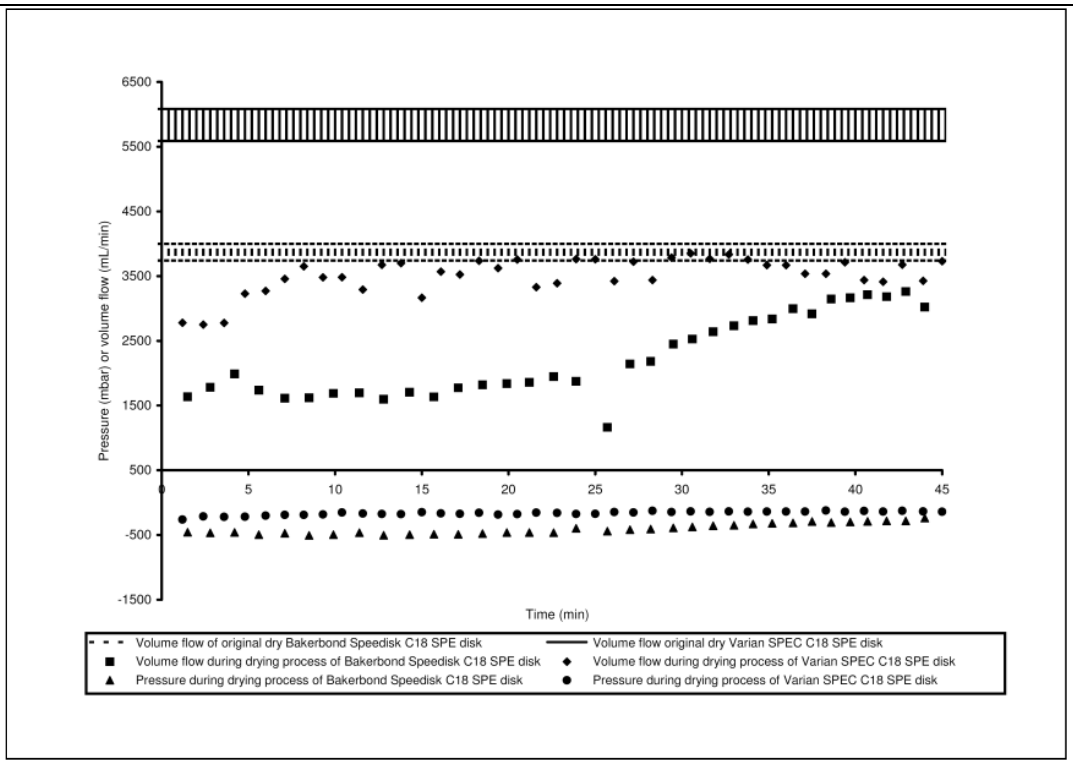

Figure 3.2: Volume flow using the original and dry C_{18} SPE disk and during the drying process of both C_{18} SPE disks of J. T. Baker and Varian Inc.

Total gas volume

From these data, it is also possible to estimate the total gas volume for a definite drying time, by plotting the gas volume against the drying time considering the increasing volume flow for both investigated extraction disks. The dependencies of the gas volumes from the drying time can well be described by polynomial regression functions (coefficient of determination > 0.99) (Chapter 7.3.1, Figure 7.1). The gradients of the functions correspond to the volume flows of the extraction disks. Therefore, it is not surprising that the needed gas volume for the drying process depends on the used SPE disk types in addition to the volume flow. For a drying time of 30 min, the total gas volume for the Varian SPEC C_{18} SPE disk amounts to 102 L and for Bakerbond Speedisk Extraction Disk C_{18} only to 56 L. In practice, the needed gas volumes are considerably smaller, because the drying time amounts only to a few minutes (3 min - 7 min [17,29-35]) in most published methods.

Drying rate

Nevertheless, in practice, it may be important to know which time period is necessary to totally dry the extraction disk. To find these out, the residual water in the extraction disk was determined by weighing the SPE disks at different drying times and for different SPE disk types (Figure 3.3). For all examined SPE disks, the water contents decrease for increasing drying time similar to the investigation of van Hout et al. [21], but with different rates for the various disk types. This effect was also observed for SPE cartridges by Chee et al. and by Molina et al., but they did not further investigate it [16,36]. Figure 3.3, shows that the Varian SPEC C_{18} SPE disk dries faster than the Bakerbond Speedisk Extraction Disk C_{18}. After a drying time of 10 min, the water content in the Bakerbond Speedisk Extraction Disk C_{18} is nearly twice as high as in the Varian SPEC C_{18} SPE disk. Only after 50 min the values converge. As also mentioned above, this is due to the construction principle of the extraction disks. However, this is not the only reason for different drying rates. The water content in the Bakerbond Speedisk Extraction Disk H_2O Phobic DVB is always smaller than in the Bakerbond Speedisk Extraction Disk C_{18}, in spite of the same construction principle. This verifies that the type of sorbent plays a role in the drying process, too. Furthermore, the amount of phase material influences the drying process as evident from the different drying rates for the Bakerbond Speedisk Extraction Disk H_2O Phobic DVB - hc and the Bakerbond Speedisk Extraction Disk H_2O Phobic DVB. The amount of phase material for the hc extraction disk is twice as large as for the non hc extraction disk. As demonstrated in Figure 3.3, at any drying time, the residual water content is always higher in the DVB – hc SPE disk than in the DVB SPE disk. However, the water content cannot be correlated to the amount of phase material. Within the first 30 min, the water content of the DVB - hc SPE disk is only 1.3 times higher in relation to the DVB SPE disk. In Figure 3.3 it is also shown that most water is evaporated after 30 min. Then, the water content is reduced further in very small steps. After a drying time of 30 min, ca. 100 µL water remained in the Varian SPEC C_{18} extraction disk. However, further tests demonstrated a strong fluctuation of the residual water despite constant drying conditions as mentioned for SPE cartridges by Kiss et al. and Gessner et al. [15,25]. The average residue of water amounts to 280(±130) µL (n = 16, RSD = 50 %) and varies between 13 and 460 µL after a drying time of 30 min for the Varian SPEC C_{18} extraction disk. The fluctuations cannot be correlated to the dry weight of the extraction disk (869±9 mg, RSD = 1 %, n = 16) for the Varian SPEC C_{18} SPE disk and therefore to the amount of phase material. This makes it very difficult to keep the content of water in the eluates constant or at a level near zero.

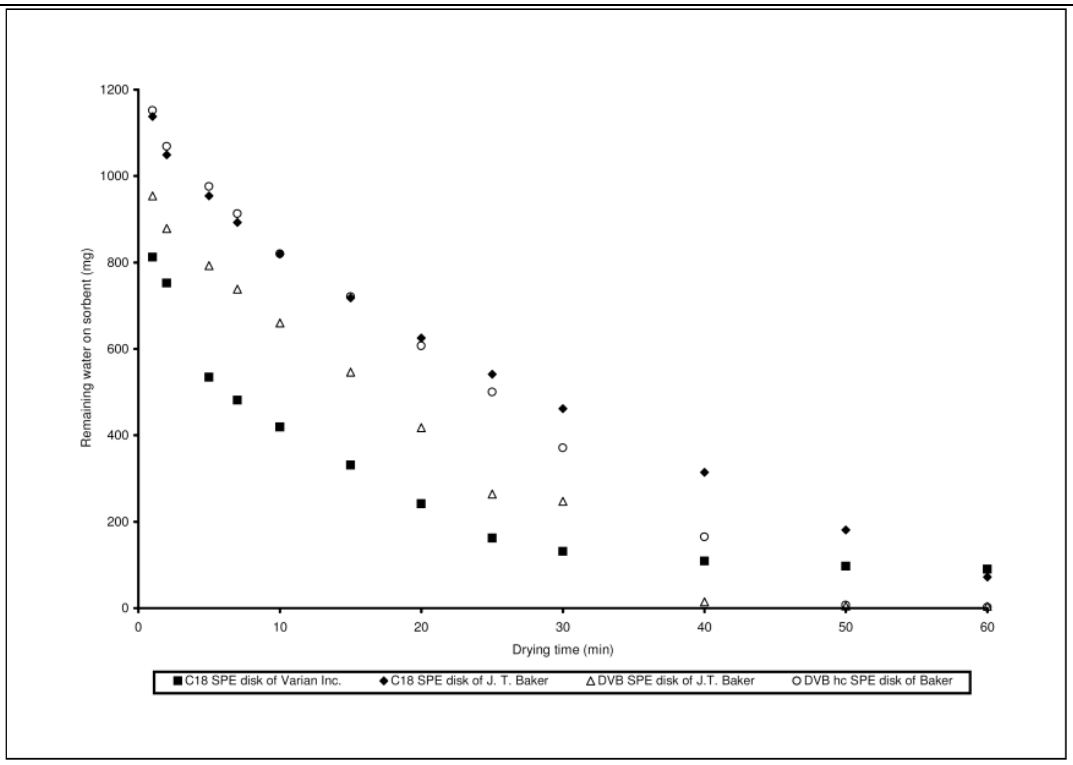

Figure 3.3: Measured amount of residual water in extraction disk during drying of different SPE disks

SPM

Furthermore, the residual water volume in the extraction disk is also influenced by SPM. During the extraction of real water samples, SPM is collected on top of the extraction disk. Then, water can also be trapped within or between sediment particles. The amount of residual water depends on the kind and amount of SPM (data not shown). Therefore, it may be necessary to extend the drying time caused by possible stronger fluctuations in presence of a larger amount of SPM [37] compared with samples without SPM.

Certainly, the disadvantages of longer drying times are the high expenditure of time [5,21] and the possible loss of volatile compounds. Volatile compounds could evaporate during the drying process and hence reduce recoveries. This was validated for the examined analytes by varying only the drying time. Indeed, for the most volatile compounds (here: substances with a partitioning coefficient log $K_{acetone - air} < 6.9$ as calculated by a polyparametric linear free energy relationships (LFER) based on Abraham's linear solvation energy relationships (LSER) theory [38,39]), i.e., trichlorobenzenes, naphthalene and acenaphthylene, lower recoveries were obtained at a longer drying time but for none of the other compounds evaporative losses were observed (Table 3.1 and Chapter 7.3.1, Table 7.3).

Table 3.1: Recoveries after different drying times using Bakerbond Speedisk Extraction Disk C_{18} and acetone (3 x 3 mL; contact time: 1 min, 5 min, 1 min) as eluent (n = 3)

Substance	7 min drying time	60 min drying time
1,3,5-Trichlorobenzene	81 ± 3 %	64 ± 3 %
1,2,4-Trichlorobenzene	87 ± 4 %	76 ± 3 %
Naphthalene	101 ± 4 %	88 ± 1 %
Hexachlorobutadiene	54 ± 1 %	48 ± 4 %
1,2,3-Trichlorobenzene	83 ± 5 %	76 ± 4 %
Acenaphthylene	93 ± 5 %	88 ± 2 %
Acenaphthene	95 ± 4 %	90 ± 4 %
Pentachlorobenzene	81 ± 3 %	76 ± 6 %
Fluorene	93 ± 5 %	93 ± 4 %
Trifluralin	88 ± 3 %	79 ± 3 %
Hexachlorobenzene	76 ± 2 %	70 ± 5 %

Thus, the drying process is influenced by the fixation of the sorbents or disk type, the pumping settings, the type of sorbent, the amount of sorbent, the SPM and of course the drying time (Figure 3.1).

3.4.2 Elution und concentration

Elution

The subsequent elution step is influenced by residual water and takes place after the drying of the SPE disk (Figure 3.1). Depending on the organic eluent used, residual water may not be fully miscible with it. This is the case, for example, for n-hexane, and can reduce recoveries and affect reproducibility [15,16,18]. In this study, five eluents, namely acetone, ethyl acetate, dichloromethane, n-hexane and tetrahydrofuran were tested. For these, no phase separation was observed in the absence of SPM. Tetrahydrofuran proved not suitable as eluent due to low recoveries (not shown) and many interfering peaks in subsequent gas chromatography. As shown in Figure 3.4, lower recoveries were determined for n-hexane compared with acetone, ethyl acetate and dichloromethane. Some of the target compounds could not be detected with n-hexane as eluent, e.g., atrazine. In comparison with n-hexane, the differences among acetone, ethyl acetate and dichloromethane as eluents are small but noticeable. They show different elution strengths for the different substance groups except for PCBs. Ethyl acetate appears to be the best eluent for the highly volatile compounds ($\log K_{acetone - air} < 6.9$), e.g., hexachlorobutadien, dichloromethane for the lower volatile analytes ($\log K_{acetone - air} > 10.8$) and acetone and ethyl acetate are comparable for all other target compounds ($6.9 < \log K_{acetone - air} < 10.8$). For example,

the best of the five eluents for the two highest volatile PAHs ($\log K_{acetone - air} < 6.9$) is ethyl acetate, for the middle volatile PAHs ($6.9 < \log K_{acetone - air} < 10.8$) is acetone and for the lower volatile PAHs ($\log K_{acetone - air} > 10.8$) is dichloromethane (Figure 3.4). The recoveries of acenaphthylene and acenaphthene with dichloromethane were only 35 % of that with acetone. Therefore, dichloromethane is not suitable for the investigation of all PAHs.

In absence of SPM, ethyl acetate seemed to be a good compromise for all investigated target compounds (Figure 3.4), including the examined pesticides. However, in presence of 500 mg certified sediment, a phase separation was observed when ethyl acetate was used and a higher vacuum was needed to suck the solvent through the SPE disk as described by Kiss et al. [15]. This is attributed to the additional trapped water in sediment, as mentioned above. To avoid the reduction of residual water by longer drying times, it is also possible to change the eluent. When using acetone instead of ethyl acetate, no problems appear due to the good miscibility of acetone and water [40]. Also, the recoveries when using acetone are similar or slightly higher than to those with ethyl acetate (Table 3.2). When processing surface water samples, the presence of SPM can not be avoided, therefore, the use of acetone instead of ethyl acetate is recommended.

Concentration

Frequently, elution is followed by a solvent concentration step to achieve an even higher enrichment factor and subsequently lower detection limits. It quickly became apparent during the implementation of the procedure that the concentration step is heavily influenced by residual water. Basically, the concentration process is limited by the subsequent analytical method due to their respective limitation of residual water in the final concentrate. Although water can be further removed from the eluate, this often is associated with harsh conditions leading to evaporative losses or the destruction of individual analytes. This could be demonstrated when concentrating the eluate to a final volume smaller than 1 mL. The residual water may also limit any solvent exchange during the concentration step, if the residual water is not miscible with the replacing organic solvent. Furthermore, the content of residual water in the eluate may alter the viscosity of the final concentrate. It may influence further evaporation of solvent and often lead to low recovery of analytical compounds.

This demonstrates that the elution as well as the following concentration step in SPE sample preparation is strongly influenced by the preceding drying step (Figure 3.1).

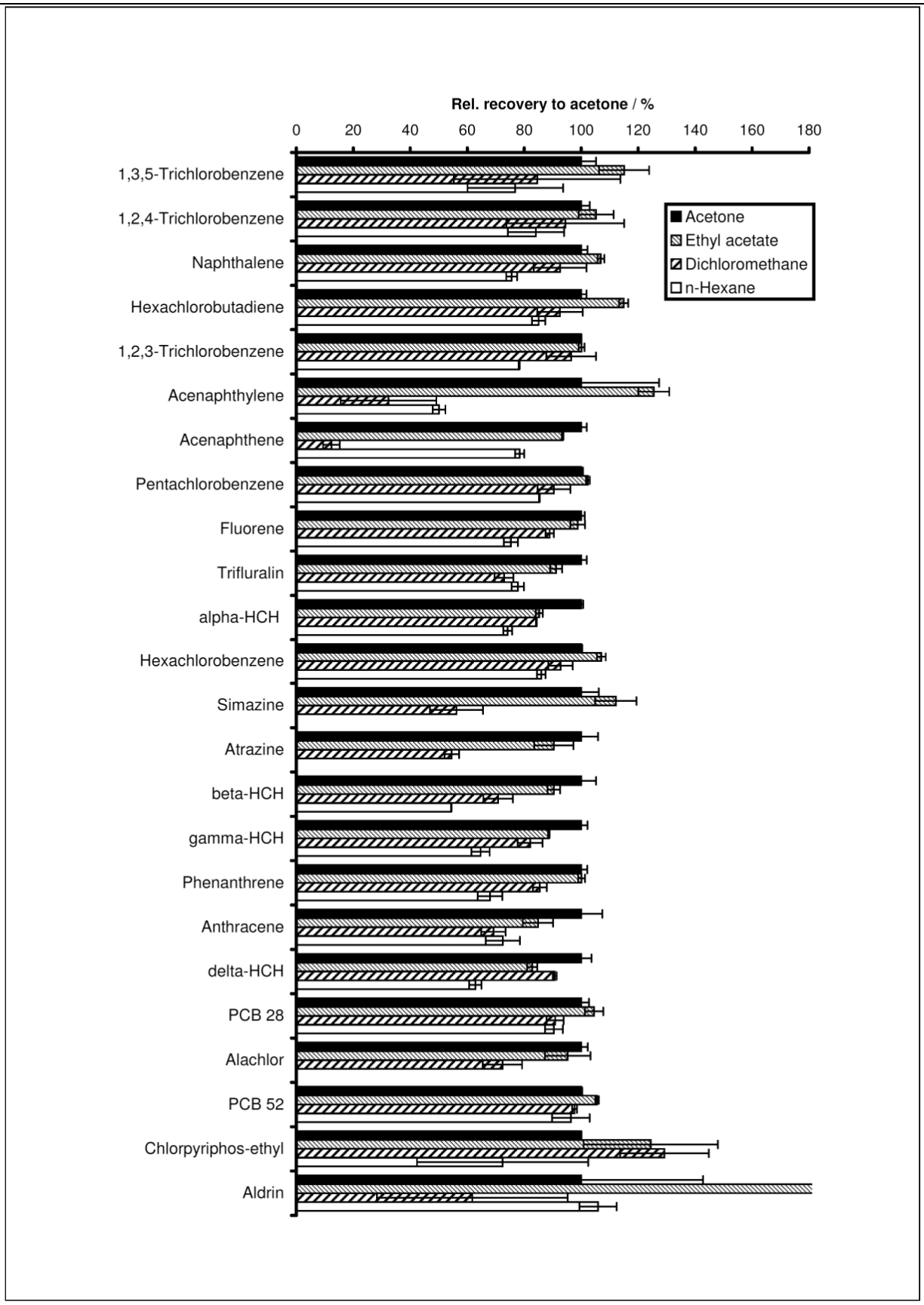

Figure 3.4: Recoveries using different organic eluents (4 x 4 mL, contact time: 5 min, each) relative to the recoveries of acetone using Varian SPEC C_{18} SPE disk and a drying time of 30 min (n = 2)

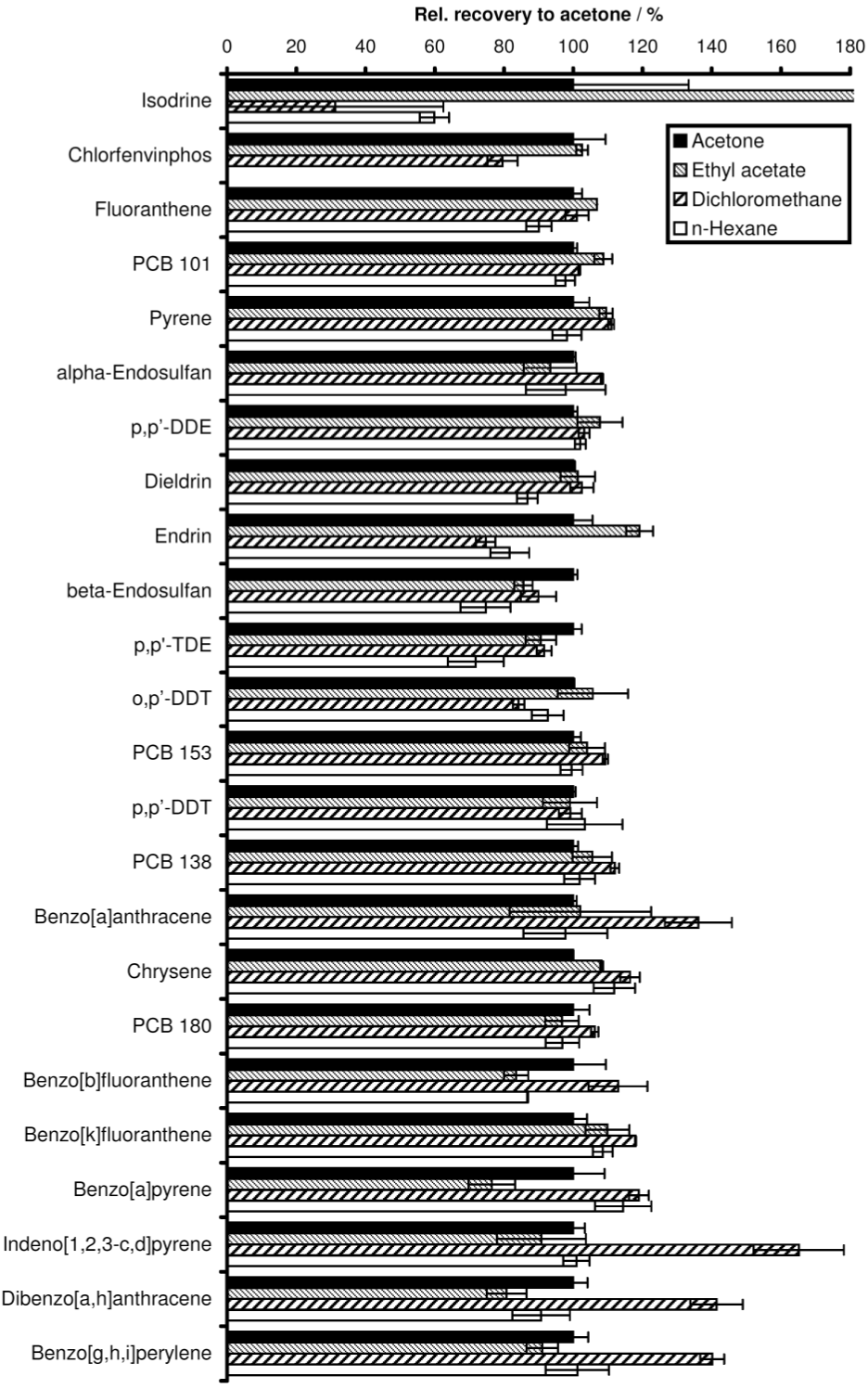

Figure 3.4: Recoveries using different organic eluents (4 x 4 mL, contact time: 5 min, each) relative to the recoveries of acetone using Varian SPEC C_{18} SPE disk and a drying time of 30 min (n = 2) (continued)

Table 3.2: SPE disk extraction of water samples spiked with 500 mg PAH-Loamy Clay 1 and eluted with ethyl acetate and acetone (4 x 4 mL, soak time: 5 min, each) using Varian SPEC C_{18} SPE disk and a drying time of 30 min

	Ethyl acetate	Acetone	Certificate
Naphthalene	129 ng/g	168 ng/g	464 ± 118 ng/g
Acenaphthylene	8 ng/g	11 ng/g	53 ± 31.9 ng/g
Acenaphthene	3 ng/g	5 ng/g	29.9 ± 19 ng/g
Fluorene	30 ng/g	32 ng/g	408 ± 125 ng/g
alpha-HCH	26 ng/g	25 ng/g	37.1 ± 9.77 ng/g
Hexachlorobenzene	16 ng/g	16 ng/g	36.5 ± 8.34 ng/g
beta-HCH	11 ng/g	12 ng/g	21.1 ± 6.05 ng/g
gamma-HCH	7 ng/g	9 ng/g	9.5 ± 2.13 ng/g
Phenanthrene	585 ng/g	618 ng/g	660 ± 102 ng/g
Anthracene	50 ng/g	59 ng/g	15 ± 9.91 ng/g
PCB 28	21 ng/g	24 ng/g	44.9 ± 9.78 ng/g
PCB 52	34 ng/g	35 ng/g	64.6 ± 12.5 ng/g
Aldrin	7 ng/g	7 ng/g	16.2 ± 3.95 ng/g
Fluoranthene	385 ng/g	388 ng/g	557 ± 87.1 ng/g
PCB 101	21 ng/g	24 ng/g	45.7 ± 9.24 ng/g
Pyrene	78 ng/g	77 ng/g	331 ± 93.4 ng/g
p,p'-DDE	11 ng/g	10 ng/g	18.8 ± 3.64 ng/g
Dieldrin	16 ng/g	15 ng/g	25.7 ± 5.9 ng/g
o,p'-DDT	18 ng/g	21 ng/g	43 ± 11.2 ng/g
PCB 153	22 ng/g	23 ng/g	41.3 ± 6.5 ng/g
p,p'-DDT	5 ng/g	4 ng/g	10.2 ± 3.74 ng/g
PCB 138	33 ng/g	35 ng/g	63 ± 10.6 ng/g
Benzo[a]anthracene	222 ng/g	259 ng/g	338 ± 78 ng/g
Chrysene	205 ng/g	214 ng/g	376 ± 38.8 ng/g
PCB 180	27 ng/g	29 ng/g	54.7 ± 8.9 ng/g
Benzo[b]fluoranthene	154 ng/g	218 ng/g	210 ± 23.9 ng/g
Benzo[k]fluoranthene	186 ng/g	192 ng/g	300 ± 34.4 ng/g
Benzo[a]pyrene	22 ng/g	26 ng/g	65.3 ± 22 ng/g
Indeno[1,2,3-c,d]pyrene	315 ng/g	321 ng/g	235 ± 35.4 ng/g
Dibenzo[a,h]anthracene	256 ng/g	271 ng/g	294 ± 34.9 ng/g
Benzo[g,h,i]perylene	57 ng/g	61 ng/g	139 ± 29.7 ng/g

3.4.3 Analysis

In this study, the eluates were analysed by GC-MS. As demonstrated above, the SPE method cannot fully prevent water from entering the GC column. However, the used Zebron ZB5 ms capillary column is a cross-linked and non-polar stationary phase, and therefore is suitable for injection of eluates containing water [23]. Carry-over is prevented due to high end temperatures of the cold injection system and the gas chromatograph (300 °C, 5 min, each). To exclude other effects caused by residual water, the same GC-MS reference solution was studied with different contents of water. The sensitivity of detection for the investigated analytes is hardly affected by the water content except for the less volatile PAH (Figure 3.5). These are strongly influenced, and the peak areas considerably decrease with increasing amount of water. This trend was also observed for other analytes, for example the trichlorobenzenes, but not as pronounced. On the other hand, the opposite was noticed as well, e.g. for triazines. For these substances, sensitivity slightly increases with an increasing amount of water. In the literature, no similar observation has been reported so far, and it cannot be explained till now. The effect could not be related to any molecular or physical parameter such as polarity, partitioning coefficient (for solvent-water or solvent-air) or vapour pressure.

It has been shown that it is difficult to prevent the fluctuation of the water content and therefore its influence on the peak area. By the used eight internal standards, deuterated PAHs and (deuterated and none deuterated) rare organic compounds, it is not possible to compensate the influence of water for the lower volatile PAHs ($\log K_{acetone - air} > 10.8$). Thus, further deuterated standards of lower volatile PAHs would be required. However, also for the other analytes, the influence of water can only partly be compensated.

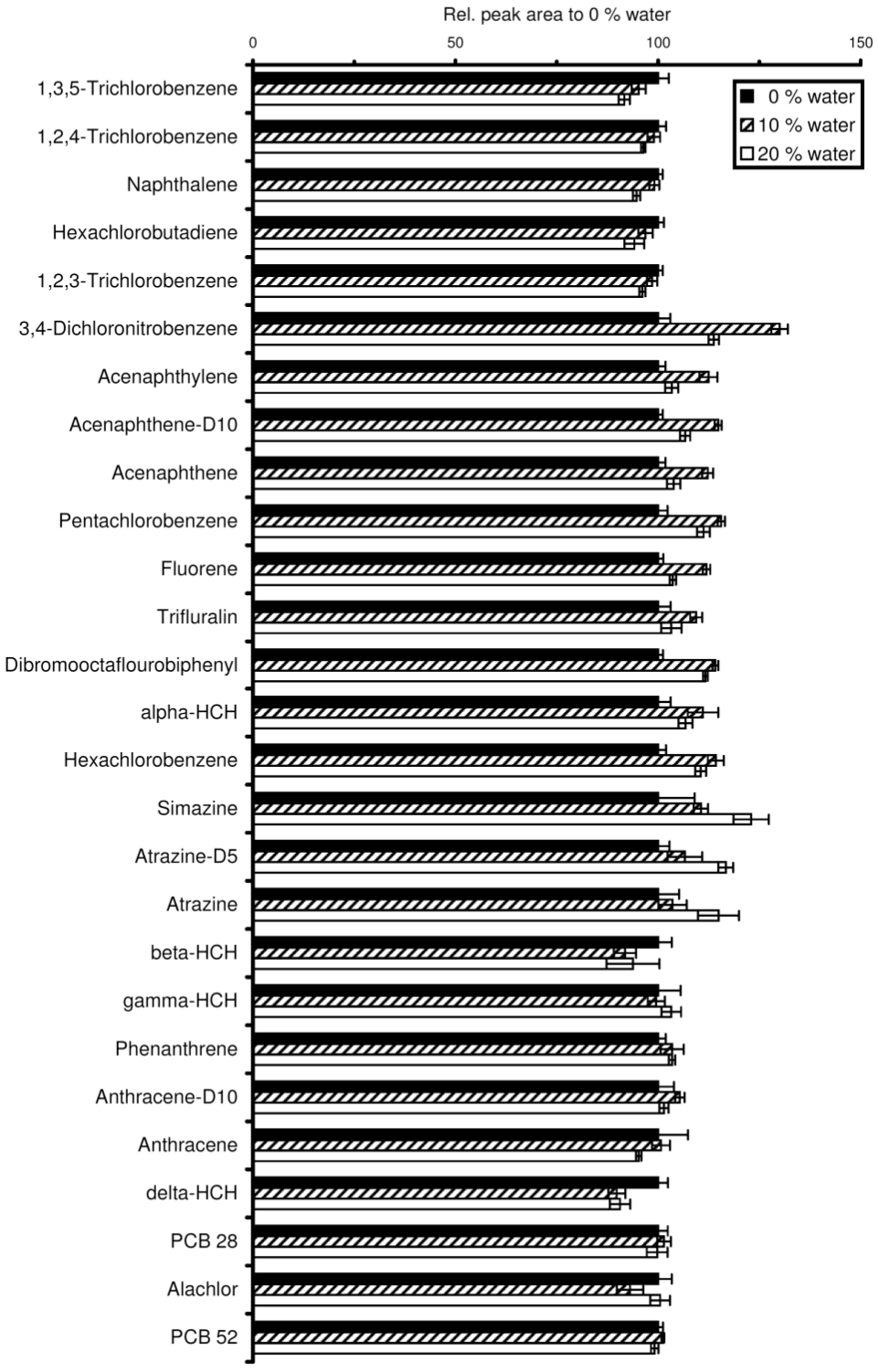

Figure 3.5: Average peak area depending on the water content of the injected solution relative to 0 % water (n = 4)

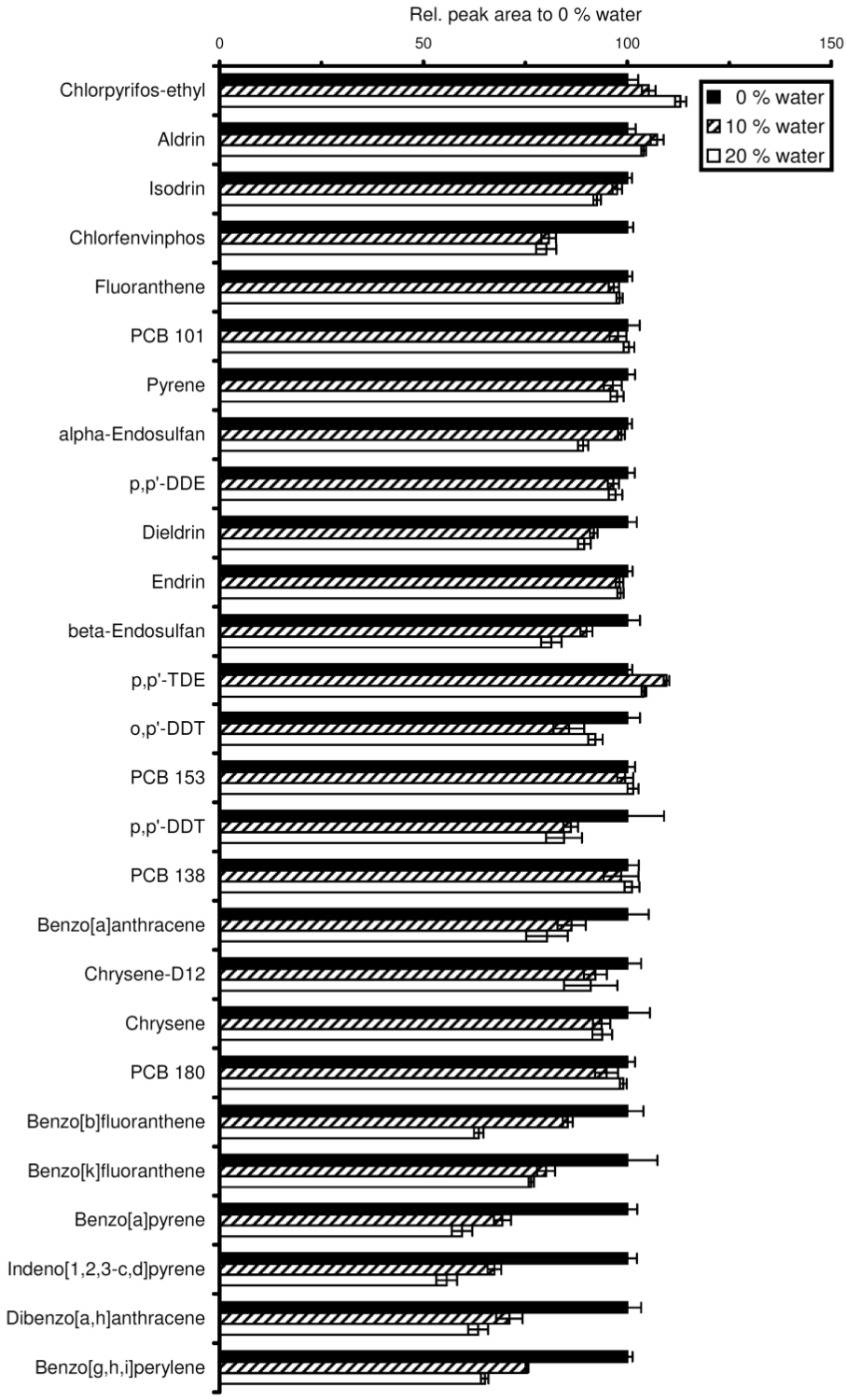

Figure 3.5: Average peak area depending on the water content of the injected solution relative to 0 % water (n = 4)

3.5 Conclusion

This study shows that residual water from the drying step has a far reaching influence on the development and the results of an analytical method. Therefore, residual water should be considered as one potential cause of failure, if a SPE based method is poorly performing.
The presented study provides a basis for further investigations and the further understanding and control of the drying process. This is of high relevance for many analytical investigations utilizing a SPE step.

3.6 Acknowledgement

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4 Multi-component trace analysis of organic xenobiotics in surface water containing suspended particular matter by solid phase extraction/gas chromatography-mass spectrometry

Redrafted from "C. Erger, P. Balsaa, F. Werres, T.C. Schmidt, Multi-component trace analysis of organic xenobiotics in surface water containing suspended particular matter by solid phase extraction/gas chromatography-mass spectrometry, J. Chromatogr., A 1249 (2012) 181", DOI 10.1016/j.chroma.2012.06.018,

4.1 Abstract

Suspended particulate matter (SPM) often disturbs the analysis of surface water by conventional methods, such as liquid-liquid extraction (LLE) or solid phase extraction (SPE), caused by insufficient extraction or by plugging. Water and SPM are therefore often separately analysed, which is associated with high expenditure of time, work and costs. Hence, SPM is partly ignored, if the fraction of sorptively bound analytes is small compared to the total analyte concentration. However, the European Water Framework Directive (WFD, Directive 2000/60/EC) requires explicitly an investigation of the whole water sample including SPM, because many priority and priority hazardous substances can sorb substantially to SPM. Therefore, an SPE disk based method was developed for the determination of 54 priority and priority hazardous pollutants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), organic chlorinated pesticides (OCPs) and other pesticides in surface water containing SPM. The developed SPE disk method allows analysis of 1 L surface water containing up to 1000 mg SPM without prior separation of SPM in about 2 h including gas chromatography-mass spectrometry (CG-MS) analysis. The limits of quantification vary in a range of 0.8 to 38 ng/L.

4.2 Introduction

Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), organic chlorinated pesticides (OCPs) and other pesticides are found in environmental samples worldwide [1-8] as a result of their persistence [2-5,9,10] and/or ubiquity [3,11]. PAHs for example are mainly formed by incomplete combustion of organic matter [3,11]. PCBs and PBDEs were primarily used as dielectric fluids in transformers and as flame retardants in polymeric materials, respectively [2,12-14]. Based on their harmful properties to humans and environment [6,9,10,15] the mentioned compound classes have either been banned or their formation, use or occurrence has been limited in many parts of the world years ago [2,3,7,9,10,12,13,15-17].

Consequently, the European Water Framework Directive (WFD, Directive 2000/60/EC) also classified a large number of such compounds as priority and priority hazardous compounds and demands the surveillance of their concentration in surface water [18,19]. However, many of these ubiquitous compounds sorb substantially on suspended particulate matter (SPM) in surface water [6,9,11,13]. For this reason, the WFD demands explicitly an investigation of the whole water sample, including the SPM [18,19].

Liquid-liquid extraction (LLE) as a typically used method for the analysis of water samples is often disturbed by SPM, caused by insufficient extraction [11,20]. Hence SPM is commonly separated from the water sample and analysed independently. Both steps, the separation and the analysis, require additional efforts. LLE as well as Soxhlet extraction, which is one possible technique for the investigation of SPM, are time-consuming and labour-intensive procedures [9,15,20,21]. Furthermore, the mentioned methods need large volumes of organic solvents in contrast to solid phase extraction (SPE) [15,21-25]. SPE is an easy, fast and efficient extraction technique, which needs small volumes of organic solvent and has the potential for automation [9,21,25]. One great disadvantage of SPE is plugging of cartridges in presence of SPM [4,8,11,15]. This could be prevented by the use of SPE disks owing to their higher cross sectional area [8,21,26]. Additional advantages by the use of SPE disks may be the smaller elution volumes and higher flow rates [8,20-22,27,28] due to the smaller particle size [21,27,29] and mass of sorbents and the mitigation of breakthrough and channelling [22,25,28]. All this may lead to higher concentration factors and therefore to lower limits of detection (LODs) [28].

Generally, in the first process step the SPE disk is conditioned by organic solvents and water, followed by extraction of the water sample, whereby SPM remains on top of the SPE disk. After a drying step, the analytes are desorbed from sorbent and SPM by an organic solvent in one single process step. After a possible concentration step the eluate is analysed.

The combination of the desorption processes from SPM and phase material allows reduction of the expenditure of time, work and costs and the amount of organic solvent. Nevertheless, SPM is still often separated from the water sample prior to analysis and SPE disk methods were designed for water samples without SPM [2,20,22,26,27,29]. McDonnell et al. investigated the decreasing flow rate caused by SPM and reported that filtration of natural water was required prior to an extraction step of several litres of water by Empore disks [30]. Typically, natural water bodies contain particulate matter at very low concentration between 1 and 100 mg/L [31,32]. In individual cases, values up to 400 mg/L [33,34] and 1000 mg/L [35] are reported in the literature. Consequently, great quantities and fluctuation of SPM also influence SPE disk methods and have to be considered during method development [36].

Several multi-residue methods were developed for water samples (I) with and (II) without SPM or (III) with prior separation of SPM. (I) EPA Method 525.1 uses SPE cartridges or disks for a multi-residue analysis of 43 organic compounds in drinking water, raw source water or drinking water in any treatment stage. The water sample is not filtered for the extraction and the recoveries for the investigated analytes vary between 15 ± 3 % (methoxychlor) and 315 ± 25 % (chlorobenzilate) [37]. EPA Method 1613 analyses 17 tetra- through octa-chlorinated dioxins and furans in water, soil, sediment, sludge, tissue and other sample matrices and recommends different procedures. One approach for aqueous samples containing less than 1 % (w/v) solids is to vacuum filter the sample through a glass-fiber filter on top of a SPE disk and subsequently to extract the filter and the disk in a Soxhlet/Dean-Stark extractor. Furthermore, it is recommended that for wastewater samples 90 or 144 mm disks are used whereas for drinking water or other samples containing low amounts of solids smaller disks are acceptable [38]. Pichon et al. developed a multi-residue analysis for 20 polar and nonpolar pesticides in surface water without previous filtration considering the national French lists of priority pesticides. To that end, they used two different methods with two different SPE disks. A divinylbenzene (DVB) polymer SPE disk was used for the extraction of polar and moderately polar compounds and a C_{18} SPE disk for the extraction of nonpolar compounds [8]. (II) An example of methods for water samples without SPM was presented by Leandro and co-workers. They demonstrated a semiautomated method for the determination of approximately 100 pesticides and transformation products in drinking water by using C_{18} SPE disks. Typical recoveries for pesticides at 0.1 µg/L in water for this

method were in the range of 72 to 120 % with relative standard deviations of less than 20 % [22]. Viana and co-workers compared SPE disk and cartridge extraction methods based on C_8 and C_{18} phase material for 44 pesticides including organochlorine, organophosphorous, carbamate, triazine and other pesticides in distilled water. They found that recoveries decreased in the following order: C_8 column, C_{18} column, C_8 disk and C_{18} disk [29]. A further example was given by Jin et al.. They developed a SPE disk method for the determination of 42 hazardous residues required by the 'Japan Positive List System' in bottled water. The recoveries of all analytes ranged between 65 and 120 % with relative standard derivations smaller than 24 % (n = 8) [20]. (III) Chiron et al. developed a multi-residue analysis for 30 pesticides and various transformation products in estuarine water and groundwater filtered prior to the pesticide enrichment. However, they stacked ten 4.6-mm extraction disks in one holder for a single extraction step and got the best results by the use of C_{18} phase material for the investigated compounds [39]. Sun et al. filtered waste water samples prior to analyte extraction. With their method the simultaneous analysis of 50 androgens was possible with overall method recoveries between 78 and 108 % [26].

None of the mentioned SPE disk methods fulfils the demands of the WFD to investigate the whole water sample including SPM for a wide range of priority and priority hazardous compounds mentioned in the WFD. Therefore, we developed a new multi-component analytical method without prior separation of SPM based on a previously established SPE disk method for PAHs [11]. The presented method allows the determination of 54 organic xenobiotics covering the substance groups of PAHs, PCBs, PBDEs, OCPs and other pesticides in surface water containing SPM up to 1000 mg/L. Thereby also natural water samples with high amount of SPM are considered. During method development the fitness for routine analysis considering the demands of the WFD was emphasized. An additional challenge was to cover the large concentration range of the annual average environmental quality standards for the investigated analytes from 0.5 to 2400 ng/L.

4.3 Experimental

4.3.1 Materials

The SPE disk apparatus of Waters and PAS Technology are identically constructed and were used for all disk types with a diameter of 47 mm and combined with a SPE manifold station by J. T. Baker. For the SPE disks with a diameter of 50 mm by J. T. Baker no additional SPE disk apparatus was necessary and the SPE manifold station could be used directly. In detail, the following disks were tested: Bakerbond-Speedisk Extraction Disk C_{18} (diameter: 50 mm, J. T. Baker), Bakerbond-Speedisk Extraction Disk C_{18} - high capacity (hc) (diameter: 50 mm, J. T. Baker), Bakerbond-Speedisk Extraction Disk H_2O Phobic DVB (diameter: 50 mm, J. T. Baker), Bakerbond-Speedisk Extraction Disk H_2O Phobic DVB - hc (diameter: 50 mm, J. T. Baker),Varian SPEC C_{18} AR SPE disk (diameter: 47 mm, Varian), Resprep Resin SPE disk (diameter: 47 mm, Restek), Resprep SPE Disk - C_{18} (diameter: 47 mm, Restek) and ENVI - C_{18} disk (diameter: 47 mm, Supelco).

4.3.2 Solvents, chemicals and standards

The following 54 xenobiotics were used as analytes in this study: alachlor, aldrin, atrazine, chlorfenvinphos, chlorpyrifos-ethyl, dieldrin, p,p'-(dichlorodiphenyl)-2,2-dichloroethylene (p,p'-DDE), 2,2-bis(o,p-chlorophenyl)-1,1,1-trichloroethane (o,p'-DDT), p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT), p,p'-(dichlorodiphenyl)dichloroethane (p,p'-TDE), alpha-endosulfan, beta-endosulfan, endrin, hexachlorobenzene, hexachlorobutadiene, alpha-hexachlorocyclohexane (alpha-HCH), beta-hexachlorocyclohexane (beta-HCH), gamma-hexachlorocyclohexane (gamma-HCH, lindane), delta-hexachlorocyclohexane (delta-HCH), isodrin, pentachlorobenzene, simazine, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, trifluralin, BDE 28 (2,4,4'-tribromodiphenyl ether), BDE 47 (2,2',4,4'-tetrabromodiphenyl ether), BDE 99 (2,2',4,4',5-pentabromodiphenyl ether), BDE 100 (2,2',4,4',6-pentabromodiphenyl ether), BDE 153 (2,2',4,4',5,5'-hexabromodiphenyl ether), BDE 154 (2,2',4,4',5,6'-hexabromodiphenyl ether), acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-c,d]pyrene, naphthalene, phenanthrene, pyrene (PAH - mix by EPA, each 100 µg/mL in acetonitril), PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180 (PCB Mix 1, each 10 ng/µL in acetone; Dr. Ehrenstorfer). Acenaphthene-D_{10}, anthracene-D_{10}, atrazine-D_5,

chrysene-D_{12}, 4,4'-dibromooctafluorobiphenyl and 3,4-dichloronitrobenzene were used as internal standards (IS) and fluoranthene-D_{10} was used as volumetric standard (VS). The purity of all used compounds was at least 97 %. The substances were purchased at Cambridge Isotope Laboratories, Dr. Ehrenstorfer, Fluka, LGC Standards, National Physical Laboratory (UK), PAH Research Institute, Riedel de Haën, SERVA or at Ultra Scientific. The used stock solutions were prepared from the analytical standards by weighing and dissolving the pure compounds in ethyl acetate or acetone (Chapter 7.4.1, Table 7.4). From these stock solutions and bought standard solutions several dilutions were prepared by the use of acetone (Chapter 7.4.1,Table 7.5). All solutions were stored at 4 °C in darkness. The solvents used for the solutions and experiments were picograde and were purchased from LGC Standards.

For method validation eight multi-component spike solutions of all analytes were prepared including internal standards (Chapter 7.4.1,Table 7.6). The analyte concentrations were varied from 0 to 50 ng/L in the sample and the IS concentrations were varied from 50 to 560 ng/L depending on their different sensitivities.

Blank water was used as sample matrix and to rinse the sample bottles. It was prepared by filtering tap water through activated carbon.

If necessary, the water samples were adjusted to a pH value between 3 and 8 by a 12.5 % aqueous hydrochloric acid and 20 % aqueous sodium hydroxide solution. They were produced by diluting 25 % aqueous hydrochloric acid (Merck) and dissolution of sodium hydroxide pellets for analysis (Merck).

As certified reference materials (CRMs) PAH Loamy Clay 1 (CRM 141-050, Lot. No: 011305), a sandy loamy fresh water sediment (pH = 6.54; particle distribution: 200 µm - 1 mm) by LGC Standards, and EC 3 sediment, a Lake Ontario Sediment (pH = 6.81; particle size: < 74 µm) for Toxic Organics from the National Water Research Institute of Canada, were used.

For the concentration and analysis step nitrogen and helium gas were used with a purity of 5.0 from Air Liquide.

4.3.3 Water samples

Blank water was used during method development. For the validation of the method surface water from river Ruhr taken at the location Styrum/Mülheim an der Ruhr, Germany on November 16th, 2010 was used in order to simulate real conditions. River water is a typical matrix for the investigation of the whole water sample as it is required in the WFD. The water had the following properties at sampling: colour: light brown; odour: earthy; temperature: 8.9 °C; pH value: 7.42 (20 °C); electrical conductivity: 268 µS/cm (25 °C); dissolved organic

carbon: 3.23 mg/L; dissolved oxygen: 10.0 mg/L; SPM: 219 mg/L; sodium: 11.7 mg/L; potassium: 2.6 mg/L; magnesium: 4.4 mg/L; calcium: 26.0 mg/L; total hardness: 4.7 °dH.
Before using the surface water, it was filtered through a glass fibre filter (pore size: 18 µm, Sartorius), homogenized and stabilized by adding 40 mg/L sodium azide (Merck) and stored at 4 °C in darkness till utilization. The pH value of the river water was 7.6 (25 °C).

4.3.4 SPE

The SPEC C_{18} AR extraction disk was conditioned twice with 6 mL acetone and twice with 6 mL blank water (contact time: 1 min). The water sample was adjusted to a pH value between 3 and 8 and spiked with 200 µL of a spike solution and/or sediment up to 1000 mg SPM not less than 60 h prior to the enrichment step to enable equilibration of sorption. Then the water sample was enriched within 20 min (50 mL/min). Additionally, the sample bottle was rinsed twice with 9 mL blank water to transport all SPM onto the extraction disk. After the SPE disk was dried for 30 min by vacuum, including the SPM, the analytes were extracted four times by 4 mL acetone (contact time: 2 min, 3 x 5 min). Then 100 µL of the VS "Fluoranthene-D_{10}, 250 µg/L" was added to the combined eluates. Subsequently, the eluate was concentrated to 1.5 mL in a gentle nitrogen stream at 40 °C (water bath) and the extract was analysed by gas chromatography-mass spectrometry (GC-MS).

4.3.5 LLE

After 1 L water was spiked with analytes and/or 500 mg sediment, 10 mL n-hexane was added to the sample and stirred for 30 min at maximum speed (magnetic stirrer RTC basic of IKA Labortechnik). Then the organic phase was separated by use of a micro separator. After 100 µL of the VS "Fluoranthene-D_{10}, 250 µg/L" was added to the extract, the extract was centrifuged for 2 min at 5000 rpm (Labofuge 200 of Heraeus Sepatech). This was necessary due to the incomplete separation of the organic phase in presence of sediment. Subsequently the organic phase was separated again and concentrated by a gentle stream of nitrogen at 40 °C (water bath) to a final volume of ca. 1.5 mL. Finally, the extract was analysed by GC-MS.

4.3.6 Soxhlet extraction

500 mg sediment was investigated by Soxhlet extraction so that comparability was given with the other sample preparation methods performed here. To that end, the sediment was Soxhlet extracted with 120 mL acetone for 9 h (ca. 90 cycles) using a 250 mL flask and a 25 x 100 mm extraction thimble (Whatman International Ltd). Subsequently the extract was cooled down to room temperature overnight. After 100 µL of the VS "Fluoranthene-D_{10}, 250 µg/L" was added, the extract was concentrated to 10 mL in a gentle stream of nitrogen at 40 °C (water bath) and was analysed by GC-MS.

4.3.7 GC-MS

All analyses were carried out on a GC 6890/MSD 5973 of Agilent Technologies equipped with a cooled injection system (CIS 4) by Gerstel. The analytes were ionised in electron impact ionization mode (EI mode, 70 eV) and detected with selected ion monitoring (SIM). The identification was achieved by the retention times and maximal four characteristic mass to charge ratios (m/z-ratios). One m/z-ratio was used for quantification (Table 4.1). The separation was performed by a Zebron ZB5 ms (30 m x 0.25 mm x 0.25 µm) capillary column by Phenomenex or a Optima®-5 ms capillary column (30 m x 0.25 mm x 0.25 µm) by Macherey-Nagel. Both columns are suitable. For method validation the Optima®-5 ms capillary column was used. Helium was used as carrier gas at a constant flow of 1.0 mL/min. After the injection of an aliquot of 1 µL of the eluate, the CIS temperature was increased with 12 °C/s from 80 °C (0 min) to 300 °C and held for 5 min. The injection was carried out in splitless mode with a splitless time of 0.5 min and subsequently purged by nitrogen. The GC oven temperature was increased with 10°C/min from 50 °C (0 min) to 300 °C and was held for 10 min (total run time: 35 min). The temperature for the transfer line and the ion source was set constantly to 280 °C and 250 °C.

Table 4.1: Retention times and SIM masses used for quantification with the Optima®-5-MS capillary column and the assignment of the internal standards (IS)

Substances	Retention time (min)	m/z-ratio for quantification	IS
1,3,5-Trichlorobenzene	8.61	180	(I)
1,2,4-Trichlorobenzene	9.29	180	(I)
Naphthalene	9.41	128	(II)
Hexachlorobutadiene	9.88	225	(I)
1,2,3-Trichlorobenzene	9.82	180	(I)
3,4-Dichloronitrobenzene (IS) (I)	12.21	191	-
Acenaphthylene	13.11	152	(II)
Acenaphthene-D_{10} (IS) (II)	13.49	164	-
Acenaphthene	13.55	153	(II)
Pentachlorobenzene	14.02	250	(I)
Fluorene	14.77	166	(II)
Trifluralin	15.64	306	(I)
4,4'-Dibromoctafluorobiphenyl (IS) (III)	15.78	456	-
alpha-HCH	16.06	219	(IV)
Hexachlorobenzene	16.30	284	(IV)
Simazine	16.44	201	(IV)
Atrazine-D_5 (IS) (IV)	16.40	205	-
Atrazine	16.44	200	(IV)
beta-HCH	16.59	219	(IV)
gamma-HCH	16.76	219	(IV)
Phenanthrene	17.03	176	(V)
Anthracene-D_{10} (IS) (V)	17.11	188	-
Anthracene	17.15	178	(V)
delta-HCH	17.20	219	(IV)
PCB 28	17.94	256	(III)
Alachlor	18.19	160	(IV)
PCB 52	18.63	292	(III)
Chlorpyrifos-ethyl	18.98	199	(IV)
Aldrin	19.04	263	(IV)
Isodrin	19.61	193	(IV)
Chlorfenvinphos	19.76	267	(IV)
Fluoranthene-D_{10} (VS)	19.85	212	-
Fluoranthene	19.89	202	(V)
PCB 101	20.33	326	(III)
Pyrene	20.42	202	(V)
alpha-Endosulfan	20.51	239	(IV)

Table 4.1: Retention times and SIM masses used for quantification with the Optima®-5-MS capillary column and the assignment of the internal standards (IS) (continued)

Substances	Retention time (min)	m/z-ratio for quantification	IS
p,p'-DDE	20.85	318	(IV)
Dieldrin	21.00	263	(IV)
Endrin	21.42	263	(IV)
beta-Endosulfan	21.56	195	(IV)
BDE 28	21.55	408	(III)
p,p'-TDE	21.62	235	(IV)
o,p'-DDT	21.72	235	(IV)
PCB 153	21.93	360	(III)
p,p'-DDT	22.33	235	(IV)
PCB 138	22.44	360	(III)
Benz[a]anthracene	23.30	228	(VI)
Chrysene-D_{12} (IS) (VI)	23.34	240	-
Chrysene	23.39	228	(VI)
PCB 180	23.66	394	(III)
BDE 47	23.71	326	(III)
BDE 100	25.28	565	(III)
Benzo[b]fluoranthene	25.79	252	(VI)
BDE 99	25.73	565	(III)
Benzo[k]fluoranthene	25.84	252	(VI)
Benzo[a]pyrene	26.57	252	(VI)
BDE 154	27.26	242	(III)
BDE 153	28.15	242	(III)
Indeno[1,2,3-c,d]pyrene	30.05	276	(VI)
Dibenzo[a,h]anthracene	30.13	278	(VI)
Benzo[g,h,i]perylene	30.99	276	(VI)

4.4 Results and discussion

4.4.1 SPE optimisation

The sample preparation method was optimized in many parameters. Specifically, influence of the sorbent, SPE disk type, conditioning volume, enrichment flow, pH value, drying time, eluent, elution volume, contact time during the conditioning and elution step, and concentration step were investigated. The influence of some of these parameters on extraction efficiency has been previously described [40].

In method development a total of eight SPE disks with different phase materials, amounts of sorbent, fixations of sorbent and companies were validated. The recoveries of the five C_{18} and the three polymeric phase materials were comparable independent of the manufacturer.

The pH value had no influence in the examined range between 3 and 8. Therefore, normally no adjustment of pH value is necessary for natural surface water.

The enrichment flow was checked in a range between 30 mL/min and 120 mL/min. The optimum of the enrichment flow is 50 mL/min. However, the volume flow is not easily reproducible due to manual handling and the enrichment flow can decrease during the sample enrichment depending on the amount and kind of SPM (Figure 4.1) at constant pressure. As Figure 4.1 shows, the average enrichment flow decreases at increasing amount of PAH – Loamy Clay 1 sediment. In contrast, the average enrichment flow is rarely influenced by the amount of EC 3 sediment. This is due to the properties of PAH – Loamy Clay 1 sediment. In the presence of PAH – Loamy Clay 1 sediment the pores of the SPE disk plugs easier and the enrichment flow is more influenced by the amount of sediment than in presence of the EC 3 sediment. This demonstrates that the average enrichment flow and therefore the extraction time cannot be predicted well even at constant operating conditions.

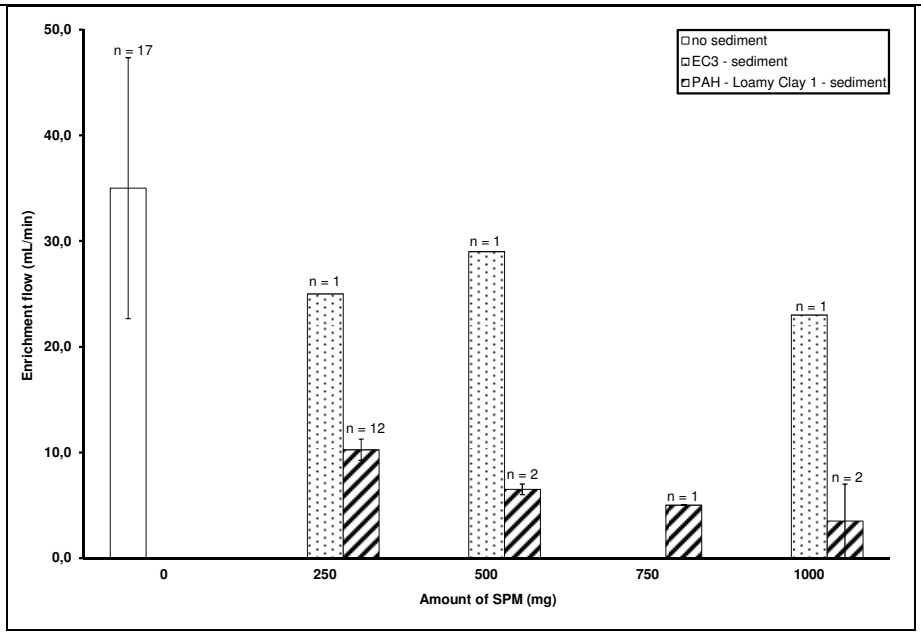

Figure 4.1: Average enrichment flow depending on amount and kind of SPM at a constant pressure; SPEC C_{18}AR Varian Inc. conditioned by 2 x 6 mL acetone and 2 x 6 mL blank water (contact time: 1 min) and loading 1 L sediment spiked sample (pH value: 7.6)

4.4.2 Method validation

Limit of quantification (LOQ)

The criteria of the WFD for the limits of quantification (LOQs) [41] have been achieved for nearly all analytes (Table 4.2). This is also the case for indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene if blank water is used instead of river water. River water was used to simulate real conditions, but the water was not totally free of the investigated analytes. A chromatogram of a blank and spiked river water sample is shown in Chapter 7.4.2 Figure 7.2 and Figure 7.3. The Directive 2009/90/EC requests that the LOQ is a multiple state of the LOD at a concentration that can be determined at an acceptable level of accuracy and precision. Here, the LOQs were calculated based on a signal to noise ratio (S/N) of six. Noise levels were determined from the average of five blank samples. The resulting LOQs range from 1.0 to 38 ng/L (Table 4.2). The WFD requires that the LOQ should be equal or below a value of 30 % of the relevant environmental quality standard [41]. The substances in Table 4.2, for which this requirement cannot be fulfilled by the presented method, are compounds where no standard method with sufficient sensitivity is available at the moment [42,43]. This is for example the case for PBDEs. They have a very low annual average environmental quality standard (AA-EQS) of 0.5 ng/L for inland water [19].

Table 4.2: Limits of quantification (LOQ) and the AA-EQS for inland waters of the WFD

Substances	LOQ S/N = 6:1 ng/L	AA-EQS Inland waters [19] ng/L	Substances	LOQ S/N = 6:1 ng/L	AA-EQS Inland waters [19] ng/L
1,3,5-Trichlorobenzene	1.8	400	PCB 101	2.4	-
1,2,4-Trichlorobenzene	1.8	400	Pyrene	15	-
Naphthalene	25	2400	alpha-Endosulfan	10	5
Hexachlorobutadiene	1.4	100	p,p'-DDE [(b)]	1.8	25
1,2,3-Trichlorobenzene	0.8	400	Dieldrin [(a)]	3.4	10
Acenaphthylene	10	-	Endrin [(a)]	3.6	10
Acenaphthene	14	-	beta-Endosulfan	13	5
Pentachlorobenzene	1.0	7	BDE 28 [(c)]	2.4	0.5
Fluorene	14	-	p,p'-TDE [(b)]	6.2	25
Trifluralin	2.2	30	o,p'-DDT [(b)]	9.0	25
alpha-HCH	6.8	20	PCB 153	3.0	-
Hexachlorobenzene	1.8	10	p,p'-DDT [(b) (d)]	2.2	10
Simazine	20	1000	PCB 138	3.0	-
Atrazine	7.0	600	Benz[a]anthracene	7.2	-
beta-HCH	3.6	20	Chrysene	11	-
gamma-HCH	3.2	20	PCB 180	3.6	-
Phenanthrene	19	-	BDE 47 [(c)]	12	0.5
Anthracene	21	100	BDE 100 [(c)]	33	0.5
delta-HCH	4.6	20	Benzo[b]fluoranthene [(e)]	9.2	30
PCB 28	1.8	-	BDE 99 [(c)]	16	0.5
Alachlor	2.8	300	Benzo[k]fluoranthene[(e)]	8.8	30
PCB 52	1.8	-	Benzo[a]pyrene	8.8	50
Chlorpyrifos-ethyl	3.0	30	BDE 154 [(e)]	36	0.5
Aldrin [(a)]	2.4	10	BDE 153 [(e)]	38	0.5
Isodrin [(a)]	16	10	Indeno[1,2,3-c,d]pyrene[(f)]	7.0	2
Chlorfenvinphos	8.2	100	Dibenzo[a,h]anthracene	7.4	-
Fluoranthene	19	100	Benzo[g,h,i]perylene[(f)]	7.2	2

(a) Sum parameter of cyclodiene pesticides Aldrin, Dieldrin, Endrin, Isodrin, (b) Sum parameter DDT isomers p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-T (AA-EQS Inland waters: 25 ng/L), (c) Sum parameter of PBDE congeners 28, 47, 99, 100, 153 and 154, (d) Additional single parameter for p,p'-DDT (AA-EQS Inland waters: 10 ng/L), (e) Sum parameter of Benzo[b]fluoranthene and Benzo[k]fluoranthene, (f) Sum parameter of Benzo[g,h,i]perylene and Indeno[1,2,3-c,d]pyrene

Recoveries and repeatability (with and without sediment)

The recoveries were determined in spiked surface water (Table 4.3) instead of ultrapure water since this provides a more realistic evaluation of method performance. The obtained values show the suitability of the method for the analysis of the whole water sample including SPM. Nearly the same recoveries were found for almost all analytes in filtered water spiked with (i) analytes, (ii) CRM sediment or (iii) CRM sediment and analytes. Exceptions are observed for some analytes strongly sorbing to the sediment, for example, fluorene. In combination with the incomplete drying of the extraction disk in presence of sediment the strong sorption may lead to low extraction efficiencies [40]. It is not clear though why this difference in recoveries is not observed for most other analytes. In contrast, the lower recoveries for the trichlorobenzenes, hexachlorobutadiene and acenaphthylene are attributed to their high volatility during the concentration step (here: substances with a partitioning coefficient $\log K_{acetone - air} < 6.0$ as calculated by a polyparameter linear free energy relationships (LFER) based on Abraham's linear solvation energy relationship (LSER) theory [35,44]). Higher recoveries for these compounds can be achieved if the eluates are measured prior to the concentration step (Chapter 7.4.3, Table 7.7). The associated higher LOQs still fulfil the demands of the WFD for these substances (Chapter 7.4.3, Table 7.8). For more than 80 % of the analytes, recoveries above 70 % were achieved including the concentration step during the sample preparation (Table 4.3). The repeatability of the whole method is indicated by the relative standard deviation (RSD) of peak area which was mostly smaller than 10 %. Only the RSDs of a few analytes for sediment spiked samples were higher. However, the certified reference values show the same uncertainty range as the determined values (Table 4.3). The method fulfils the criteria of the WFD that an applied method of analysis has to be based on an uncertainty of measurement ≤ 50 % (k = 2) estimated at the level of relevant environmental quality standards [41].

Table 4.3: Recovery in surface water spiked with analytes (27.5 ng/L), sediment (PAH-Loamy Clay 1, 250 mg) or analytes and sediment (27.5 ng/L analytes + PAH-Loamy Clay 1, 250 mg); n = 5

Substances	Recovery Analytes %	Recovery Sediment %	Recovery Analytes and sediment %	Certified reference value for sediment ng/g
1,3,5-Trichlorobenzene	41 ± 7	< LOD	50 ± 3	-
1,2,4-Trichlorobenzene	56 ± 6	< LOD	65 ± 3	-
Naphthalene	97 ± 7	65 ± 5	74 ± 3	464 ± 118
Hexachlorobutadiene	46 ± 4	< LOD	43 ± 3	-
1,2,3-Trichlorobenzene	60 ± 4	< LOD	63 ± 3	-
3,4-Dichloronitrobenzene (IS)	66 ± 8	67 ± 9	78 ± 3	-
Acenaphthylene	65 ± 6	81 ± 4	86 ± 2	53.4 ± 31.9
Acenaphthene-D_{10} (IS)	80 ± 5	77 ± 7	89 ± 5	-
Acenaphthene	88 ± 8	≤ LOQ	84 ± 4	29.9 ± 19.0
Pentachlorobenzene	71 ± 3	< LOD	73 ± 2	-
Fluorene	97 ± 5	≤ LOQ	24 ± 2	408 ± 125
Trifluralin	65 ± 4	< LOD	77 ± 4	-
4,4'-Dibromoctafluorobiphenyl (IS)	77 ± 4	65 ± 11	75 ± 4	-
alpha-HCH	80 ± 5	99 ± 11	85 ± 7	37.1 ± 9.77
Hexachlorobenzene	75 ± 4	90 ± 13	77 ± 5	36.5 ± 8.34
Simazine	81 ± 8	< LOD	107 ± 12	-
Atrazine-D_5 (IS)	76 ± 5	80 ± 13	78 ± 6	-
Atrazine	84 ± 7	< LOD	84 ± 6	-
beta-HCH	80 ± 2	106 ± 7	82 ± 6	21.1 ± 6.05
gamma-HCH	81 ± 4	≤ LOQ	80 ± 4	9.5 ± 2.13
Phenanthrene	113 ± 8	87 ± 2	90 ± 4	660 ± 102
Anthracene-D_{10} (IS)	67 ± 5	70 ± 3	73 ± 3	-
Anthracene	86 ± 7	≤ LOQ	115 ± 8	15.0 ± 9.91
delta-HCH	98 ± 8	< LOD	99 ± 8	-
PCB 28	80 ± 2	81 ± 4	86 ± 5	44.9 ± 9.78
Alachlor	82 ± 8	< LOD	78 ± 6	-
PCB 52	80 ± 3	87 ± 6	86 ± 4	64.6 ± 12.5
Chlorpyrifos-ethyl	77 ± 2	< LOD	77 ± 4	-
Aldrin	69 ± 4	91 ± 9	78 ± 5	16.2 ± 3.95
Isodrin	73 ± 3	< LOD	82 ± 7	-
Chlorfenvinphos	71 ± 4	< LOD	49 ± 6	-
Fluoranthene	100 ± 3	85 ± 6	91 ± 4	557 ± 37.1
PCB 101	79 ± 4	85 ± 7	86 ± 5	45.7 ± 9.24
Pyrene	93 ± 2	31 ± 2	48 ± 2	331 ± 93.4
alpha-Endosulfan	100 ± 6	≤ LOQ	89 ± 9	14.2 ± 3.91

Table 4.3: Recovery in surface water spiked with analytes (27.5 ng/L), sediment (PAH-Loamy Clay 1, 250 mg) or analytes and sediment (27.5 ng/L analytes + PAH-Loamy Clay 1, 250 mg); n = 5 (continued)

Substances	Recovery Analytes %	Recovery Sediment %	Recovery Analytes and sediment %	Certified reference value for sediment ng/g
p,p'-DDE	81 ± 4	110 ± 6	93 ± 7	18.8 ± 3.64
Dieldrin	87 ± 5	104 ± 5	95 ± 5	25.7 ± 5.90
Endrin	98 ± 4	≤ LOQ	87 ± 7	10.4 ± 6.31
beta-Endosulfan	76 ± 4	< LOD	79 ± 6	-
BDE 28	80 ± 4	< LOD	83 ± 6	-
p,p'-TDE	72 ± 4	< LOD	80 ± 4	-
o,p'-DDT	67 ± 4	81 ± 11	74 ± 4	43.0 ± 11.2
PCB 153	77 ± 4	≤ LOQ	120 ± 6	41.3 ± 6.5
p,p'-DDT	58 ± 5	90 ± 7	61 ± 4	10.2 ± 3.74
PCB 138	76 ± 5	88 ± 8	86 ± 5	63.0 ± 10.6
Benz[a]anthracene	84 ± 5	54 ± 5	67 ± 6	338 ± 78.6
Chrysene-D_{12} (IS)	78 ± 5	81 ± 7	85 ± 7	-
Chrysene	85 ± 3	75 ± 6	81 ± 4	376 ± 38.8
PCB 180	77 ± 5	89 ± 8	88 ± 6	54.7 ± 8.9
BDE 47	84 ± 6	< LOD	91 ± 8	-
BDE 100	83 ± 6	< LOD	95 ± 10	-
Benzo[b]fluoranthene	89 ± 7	75 ± 7	87 ± 6	210 ± 23.9
BDE 99	97 ± 9	< LOD	92 ± 15	-
Benzo[k]fluoranthene	82 ± 5	58 ± 5	65 ± 2	300 ± 34.4
Benzo[a]pyrene	58 ± 4	≤ LOQ	58 ± 3	65.3 ± 22.0
BDE 154	81 ± 4	< LOD	85 ± 7	-
BDE 153	82 ± 7	< LOD	80 ± 10	-
Indeno[1,2,3-c,d]pyrene	81 ± 9	61 ± 8	89 ± 6	235 ± 35.4
Dibenzo[a,h]anthracene	79 ± 4	80 ± 9	88 ± 5	294 ± 34.9
Benzo[g,h,i]perylene	73 ± 3	52 ± 5	65 ± 6	139 ± 29.7

(IS) internal standard, < LOD: analyte concentration is smaller than the limit of detection, ≤ LOQ: analyte concentration is smaller than the limit of quantification, -: no information available

Calibration (with and without sediment)

The method calibration was performed in a concentration range of 5 to 50 ng/L. To that end, surface water was spiked with the 54 investigated analytes. For all substances a linear correlation was found, indicated for almost all analytes by correlation coefficients (r) above 0.99 (Chapter 7.4.4, Table 7.9). The few r values below 0.99 can be traced back to the sample preparation, because r was greater than 0.99 for all analytes for the GC-MS method (data not shown).

The method was also validated in the case that sediment is present in the water sample. To that end, water samples were spiked with up to 1000 mg CRM (PAH Loamy Clay 1). A picture (Chapter 7.4.4, Figure 7.4) of the sediment spiked samples demonstrates that the visual impression can deceive in relation to the mass concentration of SPM and depends on the kind of sediment present. For sediment spiked water samples the r values are also above 0.99 for nearly all investigated analytes at continuously increasing amounts of sediment (Chapter 7.4.4, Table 7.9). However, the analyte concentration is partly significantly higher than the calibration range for the sediment spiked samples (compare Table 4.3 and Chapter 7.4.4, Table 7.9). Moreover, the lower limit of the calibration range is higher than 5 ng/L because of higher LOQs (Table 4.2). The results demonstrate that the linear range could be substantially greater than the investigated range.

4.4.3 Real sample

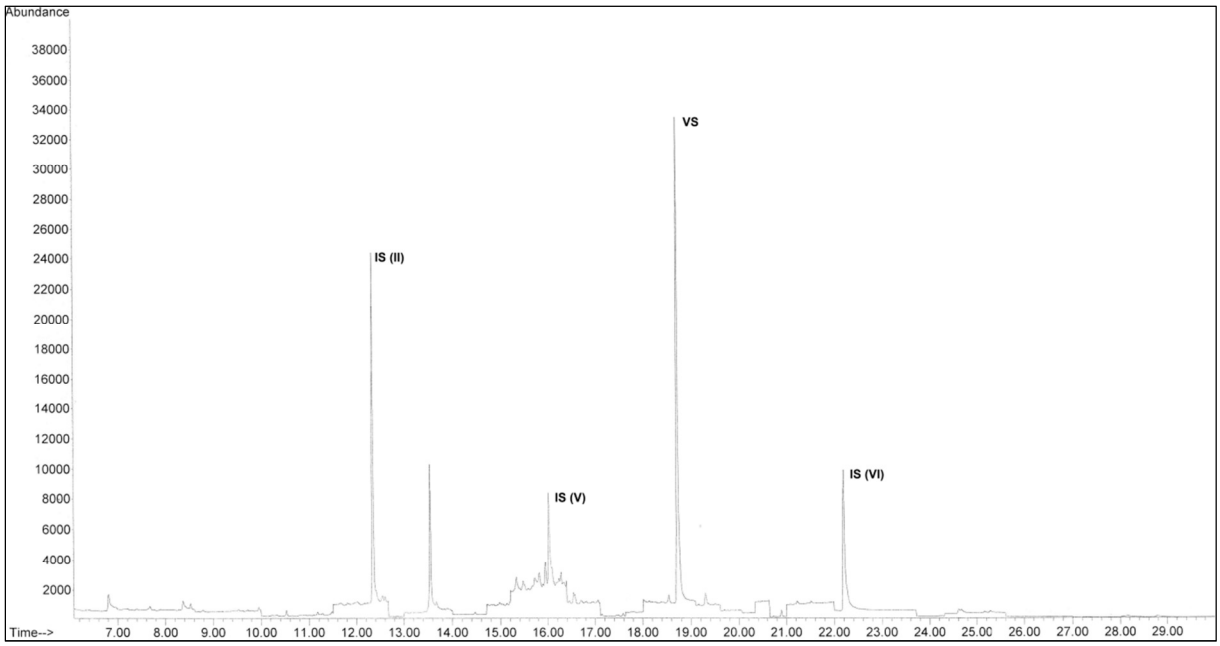

Figure 4.2: Total ion current chromatogram of unfiltered river water from river Ruhr in SIM mode

In order to demonstrate that the method also works for real samples an unfiltered water sample from river Ruhr was measured. In this case only the three PAHs were used as internal standards. Figure 4.2 shows a chromatogram of this sample. For none of the investigated analytes concentrations above the LOQ were detected. In surveillance of surface waters according to the WFD, many samples will not contain quantifiable amounts of analytes. The frequent negative findings further underline the need for a multi-component method to reduce efforts and costs of analysis.

4.4.4 Comparison with alternative methods

The performance of the developed SPE disk method was demonstrated by comparison with alternative sample preparation methods. To that end, water samples spiked with analytes, sediment or both were investigated in parallel by LLE, Soxhlet extraction and the developed SPE disk method (Chapter 7.4.5, Table 7.10). In Figure 4.3, the recoveries of the different methods for the extraction of 500 mg certified EC 3 sediment are compared. Corroborating the observation of Werres et al. for PAHs [11], the SPE disk method performs significantly better than LLE. Observed a certified concentrations agree very well for the SPE disk method as indicated by the slope of the linear fit in Figure 4.3 of almost 1. For nearly all analytes significantly lower recoveries were determined for the LLE method, resulting in a slope of the linear fit in Figure 4.3 of less than 0.4. In contrast, Soxhlet extraction on average leads to overestimations of the concentrations, especially for the higher concentrated analytes, is resulting in a slope of the linear fit in Figure 4.3 of 1.3. Furthermore, the results shown in Figure 4.3 demonstrate that the method works also for other sediments than the mainly investigated sandy loamy fresh water sediment, PAH Loamy Clay 1 (Comparison of results summarized in Table 4.3 and Chapter 7.4.5, Table 7.10).

The performance of the developed method was compared with multi-residue methods described in the literature. Due to different definitions of LOQ, it is not meaningful to compare the determined LOQs with those in the literature. Therefore, only the recoveries were considered. These agree well with those mentioned by Pichon et al. [8], Jin et al. [20], Leandro et al [22], Viana et al. [29] and by the EPA Method 525.1 [37]. However, these studies were more limited with regard to the scope of analytes considered in comparison with the multi-component method presented here. PAHs, PBDEs and PCBs have not been considered in the mentioned SPE disk based methods. The SPE disk method introduced here therefore substantially extends previous methods (i) by the spectrum of analytes, which is tailored to the requirements of the WFD, and (ii) by explicitly addressing water samples containing SPM without its prior separation.

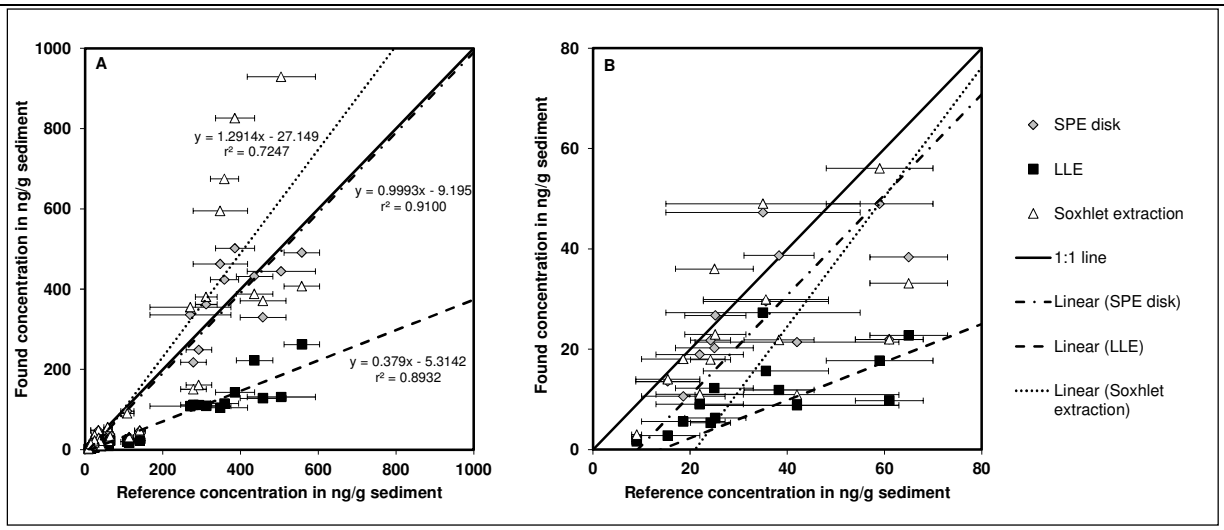

Figure 4.3: Comparison of SPE disk, LLE and Soxhlet extraction method for extraction of 500 mg certified EC 3 sediment. The limits of uncertainty of the certified values are illustrated as error bars. Relative standard deviations for found concentrations were omitted to increase legibility. Panel B is a detailed view of the smaller concentration range in panel A. All values are given in Chapter 7.4.5, Table 7.10)

4.5 Conclusions

The SPE method presented here is suitable for the analysis of 54 xenobiotics in surface water containing SPM up to 1000 mg. 1 L of the water sample is analysed in one sample preparation step in ca. 2 h including GC-MS analysis. High recoveries and low LOQs were achieved by the developed method and at the same time the method could reduce time, work, cost and the amount of organic solvents compared to conventional methods such as LLE or Soxhlet extraction. Furthermore, it is possible to apply the method to further analytes and substance groups and to integrate them in the existing method, for example, dioxins and nitrobenzene that are mentioned in the German implementation of the WFD [42] and to combine the developed sample preparation method with other methods of analysis such as high performance liquid chromatography after solvent exchange. On-going work focusses on a further improvement of LOQs by the use of large volume injection GC-MS.

4.6 Acknowledgement

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4.7 References

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5 Determination of organic priority pollutants in the low ng/L-range in water by solid phase extraction disk combined with large volume injection/gas chromatography-mass spectrometry

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5.1 Abstract

Polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) in the low ng/L-range in water were enriched by solid phase extraction (SPE) disks and their concentration determined by large volume injection/gas chromatography-mass spectrometry (LVI/GC-MS). One advantage of using SPE disks in comparison with SPE cartridges is that suspended particulate matter (SPM) does not have to be separated prior to the enrichment step, which saves time and effort. To increase the sensitivity of the method the SPE disk procedure was combined with LVI/GC-MS, which has not been reported so far for water analysis. The method was calibrated in ranges from 0.25 to 2.5 ng/L and from 2.5 to 25 ng/L. The average recovery was 76 % at an analyte concentration of 2.5 ng/L. The limits of quantification (LOQs), defined at a signal to noise ratio of 6:1, reach from 0.1 to 24.0 ng/L and are up to 400 times lower than previously reported in water analysis. By the developed SPE/LVI/GC-MS method, it is possible to investigate the whole water sample without prior separation of the SPM within 2 h including GC-MS analysis.

5.2 Introduction

One of the biggest advantages of solid phase extraction (SPE) disks in water analysis is that no prior separation step is necessary for the investigation of surface water containing suspended particulate matter (SPM). Due to the higher cross sectional area in contrast to SPE cartridges, SPE disks rarely tend to plug in presence of SPM [1-3]. Therefore, no additional efforts are necessary to separate SPM and time and work can be saved [4]. Other advantages of SPE disks compared with SPE cartridges mentioned in literature are mitigation of breakthrough and high flow rates [1, 2, 5], which allow the extraction of high sample volumes [5]. This is again linked with high enrichment factors and low limits of detection (LODs), without the risk of channelling [5].

Generally, after conditioning the SPE disk by an organic solvent and water, the whole water sample is enriched on the SPE disk, without prior separation of SPM. Thereby the SPM remains on top of the extraction disk. Following a subsequent drying step, the analytes are eluted from the phase material and the SPM by an organic solvent in one step. After a potential volume reduction of the solvent, the extract can be analysed.

Due to the low concentration of organic compounds in the aqueous environment, sensitive methods are required for their determination. One possible way is to combine SPE disk enrichment with a large volume injection (LVI)/gas chromatography-mass spectrometry (GC-MS) method. In contrast to the usual injection volume of a few µL much larger volumes of extract are injected into the analytical device and consequently the sensitivity of the analytical method can be principally increased.

Despite simplicity of this approach, in literature only one method for water analysis is documented, which combines SPE disks (diameter $\geq$ 47 mm) with LVI/GC. Steen et al. linked a LVI/GC-ion trap tandem MS method (injection volume: 40 µL) with a SPE disk sample preparation procedure by using styrene divinylbenzene (DVB) extraction disks for the investigation of five pesticides, including atrazine. The study focused on increasing sensitivity by using MS/MS and different ionisation modes [6]. In contrast, with regard to sample preparation the authors merely mentioned the used method without any validation. Thus, the study presented here is the first that details the validation of a SPE disk/LVI/GC-MS method.

Although attractive, there are also some limitations of LVI. The noise level and matrix-based interferences and therefore the LODs increase by increasing injection volume [7-9]. To suppress these effects additional efforts during the sample preparation, such as pure solvents and clean-up procedures are necessary [7, 8]. Furthermore, loss of analytes associated with low recoveries can

occur because analytes are carried along during solvent elimination via the split vent, by strong adsorption onto the packing material or by degradation in the liner [8, 10-12]. These drawbacks can be overcome by closing the vent shortly before the solvent elimination is finished, by adding a solvent with higher boiling point (also called keeper or co-solvent) or by using empty liners, liners with suitable adsorption material or with smaller inner diameter [8]. Wei et al. suggested to set the programmable temperature vaporizer (PTV) temperature at least to 10 °C below the boiling point of the solvent, to reduce the partial loss of polybrominated diphenyl ether (PBDE) congeners during solvent elimination, in particular of the lower PBDEs, and the thermal degradation at higher temperature [13]. A “dirty” liner may lead to degradation and discrimination of analytes, as described by Tollbäck et al. for heavy PBDEs. Correspondingly, they changed the liner after 100 to 200 injections [14]. Zhao et al. changed the liner already after 100 injections of sample extracts [9]. They determined halogenated persistent organic pollutants, such as PBDEs and polychlorinated biphenyls (PCBs), in soil, sediment and fish tissue [14] in contrast to Tollbäck et al., who investigated air samples [9]. Moisture in the sample extract may have negative influences on GC-MS analysis as well, e.g. on the ionization process [15]. The occurrence of residual water and its effect on GC-MS measurement for the SPE disk method used in this study were already investigated previously [16].

Based on the experiences and results of a previous work, which investigated the determination of 54 xenobiotics in surface water without prior separation of up to 1000 mg/L SPM by a SPE disk/GC-MS procedure [17], in the present study a SPE disk/LVI/GC-MS method was developed to reduce further the limits of quantification (LOQs). The here described multiple compound method was validated for 24 analytes in water in the low ng/L-range and covered the substance groups of the PBDEs, PCBs, polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs).

5.3 Experimental

5.3.1 Materials

For the SPE procedure the Varian SPEC C_{18} AR SPE disks (diameter: 47 mm) by Varian were used in combination with a SPE disk holder of Waters and a SPE vacuum manifold station by J. T. Baker.

For GC-MS method development empty, deactivated, single-baffled and multi-baffled glass liners and glass liners with silanized glass wool were tested in a cooled injection system (CIS) 4 from Gerstel.

5.3.2 Solvents, chemicals and standards

In this study the following 24 target compounds were investigated: aldrin, dieldrin, 2,2-bis(o,p-chlorophenyl)-1,1,1-trichloroethane (o,p'-DDT), p,p'-(dichlorodiphenyl)dichloroethane (p,p'-TDE), endrin, alpha-endosulfan, beta-endosulfan, isodrin, BDE 28 (2,4,4'-tribromodiphenyl ether), BDE 47 (2,2',4,4'-tetrabromodiphenyl ether), BDE 99 (2,2',4,4',5-pentabromodiphenyl ether), BDE 100 (2,2',4,4',6-pentabromodiphenyl ether), BDE 153 (2,2',4,4',5,5'-hexabromodiphenyl ether), BDE 154 (2,2',4,4',5,6'-hexabromodiphenyl ether), benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene, indeno[1,2,3-c,d]pyrene (PAH - mix by EPA, each 100 µg/mL in acetonitril), PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180 (PCB Mix 1, each 100 ng/L in acetone; Dr. Ehrenstorfer). In addition, PCB 208 (Ultra Scientific) was used as volumetric standard (VS). The purity of all used substances was at least 97 %. They were purchased from Cambridge Isotope Laboratories, Dr. Ehrenstorfer, Fluka, LGC Promochem, National Physical Laboratory (UK), PAH Research Institute, Riedel de Haën, SERVA or Ultra Scientific.

The used stock solutions were prepared by weighing and solving the standards in a defined volume of solvent or were purchased from mentioned suppliers (Chapter 7.4.1, Table 7.4). All other used solutions were made by diluting the stock solution or their dilutions in a defined volume of acetone (Chapter 7.4.1, Table 7.5 and Chapter 7.5.1, Table 7.11 to Table 7.13). The total method was validated in concentration ranges from 0.25 to 2.5 ng/L and from 2.5 to 25 ng/L. For every concentration range seven spike solutions were used (Chapter 7.5.1, Table 7.13). Up to their use, all solutions were stored in darkness at 4 °C.

PCB 208 and fluoranthene-D_{10} were used as VSs and were combined in one solution (Chapter 7.4.1, Table 7.5 and Chapter 7.5.1, Table 7.11 and Table 7.12). The combination of the two VSs

enables to connect a single sample preparation step with two subsequent analytical methods with different sensitivities and allows to cover a large concentration range. In this case, the SPE disk method can be combined with a GC-MS method with an injection volume of 1 µL [17] and 175 µL, whereby the latter method is described in the presented study and PCB 208 was used as VS.

All solvents used for the experiments were picograde and were purchased from LGC Promochem.

The used nitrogen and helium gas had a purity of 5.0.

5.3.3 Blank water

For the experiments, tap water filtered through activated carbon (blank water, pH = 6.15) was used. This water was absolutely free of analytes and was used to prove fitness of the developed method. The water was also used to rinse the sample bottles after the extraction step.

5.3.4 Solid phase extraction (SPE)

SPE was performed as described in the previous study [17] and is briefly described here. For method validation, the water sample was spiked with 200 µL of a spike solution 24 h before the sample preparation was implemented to enable equilibration. In the beginning, the SPEC C_{18} AR extraction disk was conditioned with acetone and blank water. Then 1 L water sample was enriched within 20 min (50 mL/min) on the SPE disk. To transfer the whole sample on the SPE disk the sample bottle was also rinsed with blank water. After drying the SPE disk for 30 min by vacuum, the analytes were extracted four times by 4 mL acetone (contact time: 2 min, 3 x 5 min). Subsequently, 100 µL of the volumetric standard (250 µg/L) was added to the combined eluates and then the eluates were concentrated to 1.5 mL in nitrogen stream at 40 °C (water bath). Finally, the extract was stored in darkness at 4 °C until it was analysed by GC-MS.

5.3.5 Gas chromatography-mass spectrometry (GC-MS)

For the analysis of the extracts, a GC 6890/MSD 5973 of Agilent Technologies equipped with a CIS 4 and a multi-purpose-sampler (MPS)-2 by Gerstel was used. During method development the injection volume, the injection speed, the injection temperature, including the holding time at the end of CIS programme, the kind of liner and the splitless time were optimised.

In the final method, 175 µL of the extract were injected with an injection speed of 0.75 µL/s and at an injection temperature of 30 °C into an empty, deactivated, single-baffled glass liner (Figure

5.1). The solvent was removed in solvent vent mode with a vent flow of 60 mL/min (gas: nitrogen). The split vent was closed 0.05 min after the MPS-2 had terminated the injection. At the same time, the CIS temperature was increased with 12 °C/s from 30 °C (0 min) to 300 °C, which was hold for 5 min. When the CIS reached a temperature of 300 °C, the GC oven temperature was increased with 10 °C/min from 50 °C (0 min) to 300 °C and was then held for 10 min. To prevent carry-over the split vent was opened again after a splitless time of 3 min with a gas flow of 20 mL/min nitrogen (Figure 5.1). The separation was performed on an Optima®-5 ms capillary column (30 m x 0.25 mm x 0.25 µm) by Macherey-Nagel. Helium 5.0 was used as carrier gas at a constant flow of 1.0 mL/min. The analytes were ionised in electron impact ionization mode (EI-mode; 70 eV) and detected in selected ion monitoring (SIM). The identification was ensured by the retention times and maximal four characteristic mass to charge ratios (m/z-ratio) of which one was used for quantification (Table 5.1). The temperature for the transfer line and the ion source were set constantly to 280 °C and 250 °C, respectively.

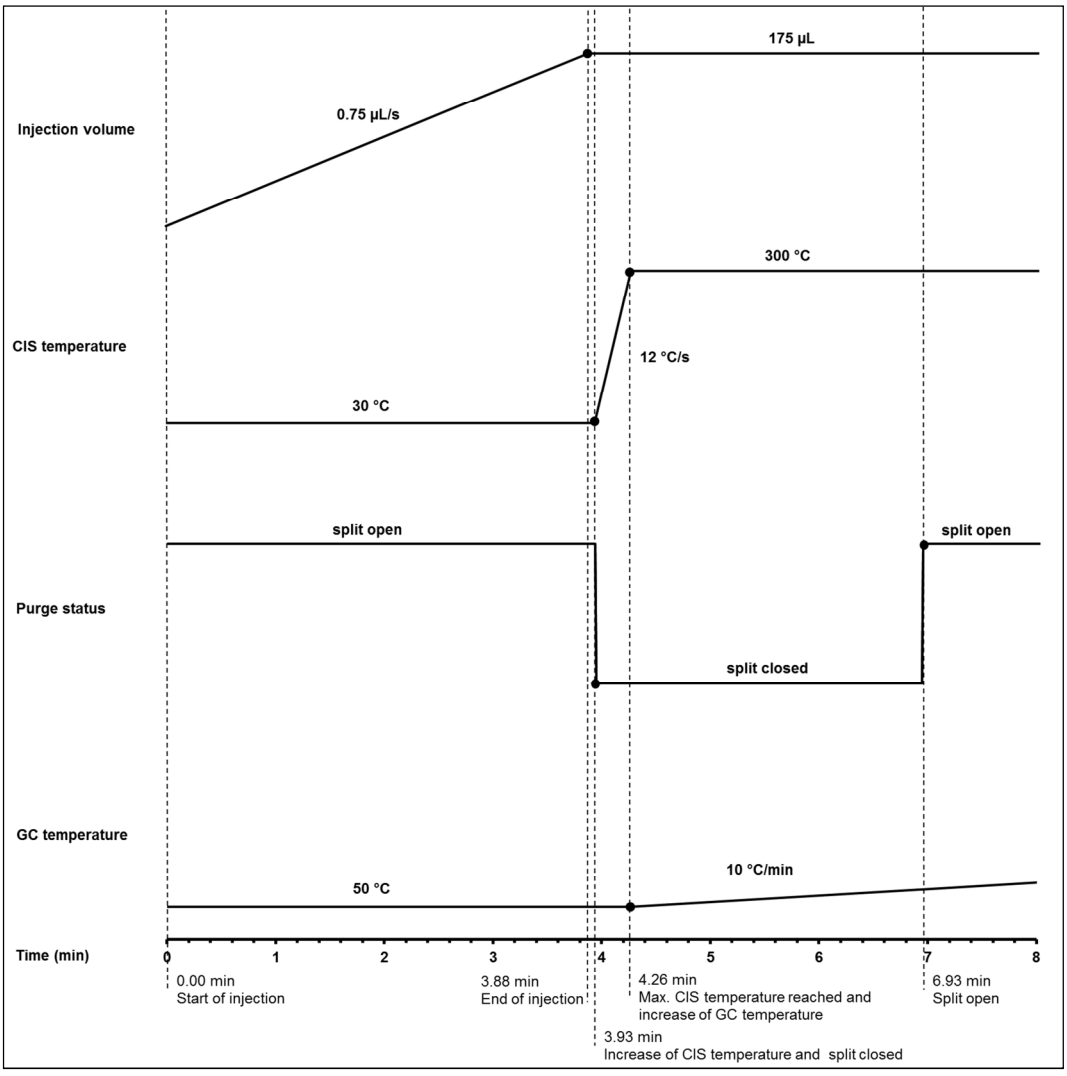

Figure 5.1: Overview on the final LVI/GC-MS method

Table 5.1: Retention times and SIM masses used for quantification and comparison of limits of detection (LODs) of the SPE-LVI/GC-MS method and the annual average-environmental quality standards (AA-EQS) for inland waters of the Water Framework Directive (WFD) and German Oberflächengewässerverordnung (OGewV)

Substance	Retention time	m/z-ratio for quantification	LOQ IUPAC (Blank + 3 SD)	AA-EQS	
				WFD [36]	OGewV [20]
	min		ng/L	ng/L	ng/L
PCB 28	18.12	256	0.1	-	0.5[f]
PCB 52	18.80	292	0.1	-	0.5[f]
Aldrin	19.22	263	0.1	10[a]	10[a, g]
Isodrin	19.79	193	0.2	10[a]	10[a, g]
PCB 101	20.51	326	0.3	-	0.5[f]
alpha-Endosulfan	20.80	239	0.3	5	5[g, h]
Dieldrin	21.19	263	1.0	10[a]	10[a, g]
Endrin	21.60	263	0.6	10[a]	10[a, g]
beta-Endosulfan	21.74	195	0.1	5	5[g, h]
BDE 28	21.73	408	0.02	0.5[b]	0.5[g]
p,p'-TDE	21.80	235	0.7	25[c]	25[c, g]
o,p'-DDT	21.88	235	0.2	25[c]	25[c, g]
PCB 153	22.10	360	0.7	-	0.5[f]
PCB 138	22.63	360	0.5	-	0.5[f]
PCB 180	23.84	394	0.5	-	0.5[f]
BDE 47	23.89	326	2.1	0.5[b]	0.5[g]
PCB 208 (VS)	25.15	394	-	-	-
BDE 100	25.49	565	5.0	0.5[b]	0.5[g]
Benzo[b]fluoranthene	26.01	252	3.3	30[d]	30[g, i]
BDE 99	25.95	565	4.2	0.5[b]	0.5[g]
Benzo[k]fluoranthene	26.06	252	3.1	30[d]	30[g, i]
BDE 154	27.56	242	12	0.5[b]	0.5[g]
BDE 153	28.49	242	3.0	0.5[b]	0.5[g]
Indeno[1,2,3-c,d]pyrene	30.47	276	5.5	2[e]	2[g, i]
Benzo[g,h,i]perylene	31.47	276	6.0	2[e]	2[g, i]

(a) Sum parameter of cyclodiene pesticides aldrin, dieldrin, endrin, isodrin, (b) Sum parameter of PBDE congeners 28, 47, 99, 100, 153 and 154, (c) Sum parameter of the DDT isomers p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-TDE, (d) Sum parameter of benzo[b]fluoranthene and benzo[k]fluoranthene, (e) Sum parameter of benzo[g,h,i]perylene and indeno[1,2,3-c,d]pyrene, (f) Including transitional waters and coastal waters; values for the water phase, (g) Without transitional waters and coastal waters – whole water sample; analogous to the WFD, (h) Sum parameter of alpha-endosulfan and beta-endosulfan, (i) The whole amount can also be determined from measurements of the fraction sorbed at suspended particulate matter, -: no information available

5.4 Results and discussion

5.4.1 LVI/GC-MS optimisation

In order to investigate the maximal injection volume possible, the injection volume was systematically increased (Chapter 7.5.2, Figure 7.5) and was finally fixed to 175 µL, due to the maximum enrichment factor achieved over the whole method including the sample preparation procedure. In order to avoid loss of sensitivity at higher injection volumes the splitless time was increased and was investigated from 3 to 7 min (Chapter 7.5.2, Figure 7.6). Finally, the splitless time was set to 3 min, caused by the small differences of peak areas between the different times. For the tested injection speeds (0.65 to 0.95 µL/min), the sensitivity showed also small differences of sensitivity and was set to 0.75 µL/s (Chapter 7.5.2, Figure 7.7). The injection temperature was varied from 20 to 50 °C and was set to the point of maximum sensitivity for most analytes at 30 °C (Chapter 7.5.2, Figure 7.8). Additionally, the holding time of the maximum temperature of the CIS was set to the point of maximum sensitivity at 5 min after it was tested between 3 and 7 min (Chapter 7.5.2, Figure 7.9). Moreover, the influence of different liner types on sensitivity was checked and was negligibly small in this case (Chapter 7.5.2, Figure 7.10). In the following, an empty, deactivated, single-baffled glass liner was used, although a multi-baffled glass liner and a glass liner with silanized glass wool are also suitable.
For all experiments of LVI/GC-MS optimisation, a solution corresponding to an analyte concentration of 25 ng/L in the water sample was used (Chapter 7.5.1, Table 7.13, “Spike VII” solution).

5.4.2 Method validation

Limit of detection (LOD)

Different definitions of LOD and LOQ used in literature complicate the comparison of different procedures and their performance. Therefore, in this study the LOD and LOQ were calculated considering different definitions (Table 5.1 and Chapter 7.5.3, Table 7.14 and Table 7.15). The LODs were determined according to IUPAC with k = 3, whereby the noise level was determined at three blank samples. The LODs varied between 0.02 and 12 ng/L (Table 5.1). Additionally, Chapter 7.5.3, Table 7.14 the LOQs were calculated by the common single to noise ratio (S/N) and the blank value method and the calibration method as described in DIN 32 645 [18] often used in Germany. The results of both methods mentioned in DIN 32 645 are not consistent. The

LOQs determined by the blank method, which is recommended by DIN 32 645, are most comparable to the LOQs calculated by the S/N (Chapter 7.5.3, Table 7.14) [18].

The definition of LOD and LOQ can also be important in association with legal standards. For example, the Water Framework Directive (WFD, 2000/60/EC) [19] and its German implementation, called Oberflächengewässerverordnung (OGewV) [20], demand that the LOQ is equal or below a value of 30 % of the relevant environmental quality standards (EQS, Table 5.1) [20, 21]. How to determine the LOQ is only further specified in the Guidance Document No. 19 of the common implementation strategy of the WFD [22]. This defines the LOQ as a multiple of the LOD at an analyte concentration that can reasonably be determined at an acceptable level of accuracy and precision and the LOD is calculated by three times the standard deviation (SD) of the blank [22]. However, this document does neither specify the multiplier nor what an acceptable level of accuracy and precision is. For example, benzo[b]fluoranthene, benzo[k]fluoranthene and PCB 28 fulfilled the requirements of WFD in the presented study only depending on the factor of multiplication of the LOD (Table 5.1).

The aim to improve the LOQs by the use of LVI (Chapter 7.5.3, Table 7.14) compared with previous injection of 1 µL [17] was achieved except for the PAHs. Direct comparison of the LOQs with literature shows that especially for the volatile compounds (retention time < 23 min) the LOQs in this study are up to 400 times lower than previously reported in water analysis (Chapter 7.5.3, Table 7.15) [23-25].

Recoveries, repeatability and linearity

The recoveries as well as the repeatability were determined for the whole method, including the SPE procedure, for an analyte concentration of 2.5 ng/L (n = 3). Due to higher LOQs than 2.5 ng/L (S/N = 6:1, Chapter 7.5.3, Table 7.14), the values could not be calculated for the late eluted analytes (retention time > 23.85 min) and therefore are not shown in Table 5.2. The recoveries vary from 42 to 114 % and are higher than 70 % for 80 % of the regarded analytes. With the exception of o,p'-DDT, all analytes in Table 5.2 fulfilled the minimum performance criteria of the WFD that the uncertainty of measurement should be smaller or equal 50 % (k = 2) estimated at the level of the relevant EQS values [21, 26]. Compared with the injection of 1 µL extract [17], for 73 % of the investigated substances the uncertainty is higher in the presented study, which is due to the ca. ten times lower analyte concentration used. Matrix effects, sorption or partial thermal degradation of the analyte during the injection catalysed by residues in the liner may all contribute to the higher uncertainty at low concentrations using LVI. Additionally, the comparison of the peak values with and without consideration of the SPE showed a

substantially influence of the sample preparation on the results despite the use of a volumetric standard (Chromatograms are shown in Chapter 7.5.3, Table 7.15), due to partly plugging of the autosampler syringe caused by eventual not totally separated phase material. Sensitivity loss over a series of GC-MS measurements was observed after significantly less than 100 injections in contrast to Tollbäck et al. and Zhao et al. [9, 14]. Degradation by the sample preparation process can be excluded by the results of previous study [17].

For all analytes reasonable working ranges could be established from LOQ (S/N = 6:1, Chapter 7.5.3, Table 7.14) to a maximum of 25 ng/L (Chapter 7.5.4, Table 7.16), with the exception of BDE 154 due to its high LOQ.

Table 5.2: Recovery in blank water spiked with analytes (2.5 ng/L) for analytes with LOQ > 2.5 ng/L; n = 3

Substance	Recovery	Relative standard deviation (RSD)
	%	%
PCB 28	64±9	14
PCB 52	61±8	13
Aldrin	42±5	11
Isodrin	80±19	24
PCB 101	73±16	22
alpha-Endosulfan	83±15	18
Dieldrin	71±13	18
Endrin	82±20	24
beta-Endosulfan	114±20	18
BDE 28	75±11	15
p,p'-TDE	85±16	18
o,p'-DDT	84±23	28
PCB 153	70±12	17
PCB 138	77±15	19
PCB 180	81±5	7

5.4.3 Comparison with alternative methods

The performance of the method was also checked by comparison with methods from literature (Table 5.3). In general, the comparison is difficult due to different experimental conditions and definitions, for example for the LOD as mentioned above. Consequently, the values in Table 5.3 are hardly comparable.

The only method mentioned in literature, which combined SPE disk with LVI/GC-MS, investigated none of the target compounds in this study [6]. All methods dealing with one substance group listed in Table 5.3 have higher or similar LODs [23, 27-30] than in the developed multi-compound procedure. Only Labadie et al. demonstrate equal or lower LODs for PBDEs by separate analysis of water phase and SPM [31] connected with several more sample preparation steps than in the method described here. Other procedures mentioned in Table 5.3 also cover several substance groups similar to the developed method. LODs of these LVI-based methods are in a similar range [24, 25, 32-35].

However, none of these other methods specifically addressed those priority pollutants of the WFD.

5.5 Conclusions

This study is one of the first investigations that combines SPE disk extraction with LVI/GC-MS and was designed to minimize the expenditure of time and work and to make the investigation of surface water containing SPM possible in one step. It is possible to achieve LOQs at the low ng/L level by the described SPE disk/LVI/GC-MS method. The aim to improve the LOQs for all 24 analytes by the use of LVI could be achieved, with the exception of the PAHs. It could be also shown that the LOQs of the developed method are lower compared with numerous methods described in literature. Further reduction of the LOQs could be reached in future by an increase of the sample volume. Additionally, in following studies the influence of the sample preparation should be investigated in more detail.

Table 5.3: Overview of performance parameter of LVI methods combined with sample preparation procedures in water analysis

Substance(s)	Sample preparation	Injection mode (Inj. Vol.)	Detection method	LOD	LOD definition	Recovery	Comment/matrix	Ref.
				ng/L		%		
16 Organophosphorus pesticides	LLME	LVI (200 µL)	GC-FPD	5-100	S/N = 3:1	38±7-117±7	Carbon blank cartridges and C_{18} disk were not suitable/ ground water	[37]
	SPE (cartridge)			1-6 ng/L		39±8-129±8 (C_{18}) 33±9-110±5 (Oasis HLB)		
5 OCPs	SPE (disk)	LVI (40 µL)	GC-MS/MS	0.5-5	S/N = 3:1	70-104	Filtered river water	[6]
24 OCPs	LLME	LVI (100 µL)	GC-MS	0.004-2.2	S/N = 3:1	92-105 (c = 2 ng/L)	River water	[27]
16 OCPs and other pesticides and herbicides as well as fluorene	MMLLE	LVI (2 µL)	HPLC-HRGC-FID or GC-MS	1.6-15	S/N = 3:1	-	-	[28]
6 PCBs	MASE	LVI (100 µL and 400 µL)	GC-MS	4-27 and 2-10	IUPAC (Blank + 3 SD)	88-100 % (river water, c = 50 µg/L)	River water, white wine and apple juice	[29]

Table 5.3: Overview of performance parameter of LVI methods combined with sample preparation procedures in water analysis (continued)

Substance(s)	Sample preparation	Injection mode (Inj. Vol.)	Detection method	LOD ng/L	LOD definition	Recovery %	Comment/matrix	Ref.
9 OCPs	SPE (cartridge)	LVI (100 µL)	GC-MS	10-50	S/N = 3:1	-	River water	[23]
9 PBDEs and tetrabromobis-phenol A	SPE (cartridges)	-	GC-MS	0.003-0.150 (river water, dissolved phase)	IUPAC (Blank + 3 SD)[1]	66.2-100.6 (pH = 2) 28.5-85.9 (pH = 8; milli-Q-water) 13.8-77.7 (pH = 2) 11.4-39.7 (pH = 8; (river water)	Separate analysis of the water phase and SPM/river water and sediment	[31]
11 PBDEs	SBSE-LD	LVI (20 µL)	GC-MS	0.3-203.4	S/N = 3:1	65.6±9.4-116.9±5.9	Ultra-pure water	[30]
31 PAHs, pesticides and herbicides	SPE (96-well plate)	LVI (50 µL)	GC-MS	18-630	SD • $t_{(N-1, 99\ \%)}$	54-369 (c =0.1 g/L)	Reagent water	[32]

Table 5.3: Overview of performance parameter of LVI methods combined with sample preparation procedures in water analysis (continued)

Substance(s)	Sample preparation	Injection mode (Inj. Vol.)	Detection method	LOD ng/L	LOD definition	Recovery %	Comment/matrix	Ref.
26 OCPs and other pesticides and herbicides as well as benzo[a]pyrene	SPE (96-well plate)	LVI (50 µL)	GC-MS	15-990	SD • $t_{(N-1, 99\ \%)}$	73±23.5-142±15.9 (laboratory reagent water, c = 0.1µg/L)	Drinking water, ground water and surface water	[33]
14 Organophosphorus pesticides, triazine, PCBs, gamma HCH, pentachlorobenzene	polysiloxane-based extraction-LD	LVI (50 µL)	GC-MS	0.1-5	IUPAC (Blank + 3 SD)	42-109	Conditions: 3.5 g NaCl + ethyl acetate/Milli-Q-water	[34]
41 PAHs, PCBs, phthalate esters, nonylphenols, bisphenol A and hormones	MEPS SPE (cartridge)	LVI (75 µL)	GC-MS	0.2-266 0.2-736	IUPAC (Blank + 3 SD)[1]	78-117 85-129	Waste water and snow	[24]
49 PAHs, PCBs, PBDEs, polybrominated biphenyls, phthalate esters and nonylphenols	SBSE MASE	TD LVI (300 µL)	GC-MS	0.03-20.4 0.1-317	IUPAC (Blank + 3 SD)[1]	81-127 81-121	Milli-Q-water	[25]

Table 5.3: Overview of performance parameter of LVI methods combined with sample preparation procedures in water analysis (continued)

Substance(s)	Sample preparation	Injection mode (Inj. Vol.)	Detection method	LOD	LOD definition	Recovery	Comment/matrix	Ref.
				ng/L		%		
75 PCB, polybrominated biphenyls, PAHs, phthalate esters, alkyl-phenols, bisphenol A and hormones	SPE (cartridge)	LVI (50 µL)	GC-MS	1-55	IUPAC (Blank + 3 SD)[1]	53-122 (blank water, after and prior derivatisation)	Derivatisation step; twice injections/ Waste water effluent	[35]
24 Organophosphorus pesticides, PAHs, PCBs and PBDEs (presented method)	SPE (disk)	LVI (175 µL)	GC-MS	0.02-12	IUPAC (Blank + 3 SD)	42±5-114±20	Filtered tap water	

FID: flame ionization detected, FPD: flame photometric detection, GC: gas chromatography, HPLC: high performance liquid chromatography, HR: high resolution, IUPAC: International Union of Pure and Applied Chemistry, LD: liquid desorption, LLME: liquid–liquid microextraction, LOD: limit of detection, LVI: large volume injection, MEPS: microextraction by packed sorbent, MASE: membrane-assisted solvent extraction, MMLLE: microporous membrane liquid–liquid extraction, MS: mass spectrometry, OCPs: organochlorine pesticides, PAHs: polycyclic aromatic hydrocarbons, PBDEs: Polybrominated diphenyl ethers, PCBs: polychlorinated biphenyls, Ref.: reference, SBSE: stir bar sorptive extraction, SD: standard derivation, S/N: single to noise ratio, SPE: solid phase extraction, TD: thermal desorption, $t_{(N-1,\ 99\ \%)}$: Student's t-value at a 99 % confidence level and N−1 degree of freedom, [1] If no signal was detected in the blank, the LOD was calculated by S/N = 3:1, -: no information

5.6 Acknowledgement

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6 General conclusions and outlook

Solid phase extraction disks (SPE disks) were used for various applications in the organic trace analysis of water from classical SPE to passive samplers. However, so far some aspects are not extensively investigated for disk SPE although the SPE technique itself is about 40 years old. Examples are storing of analytes on SPE disks, automatization of disk SPE and occurrence as well as consequences of residual water after the extraction step. Partly these points have been answered by the presented study.

The occurrence of residual water after the sample extraction could be attributed to the fixation of the sorbent, the phase material, the amount of sorbent, the pumping settings, the duration of the drying process and suspended particulate matter (SPM) containing in the sample. Admittedly, the results can only be basis for further studies. Although the influencing parameters can be specified by this study, the causal characteristics of the parameters were not isolated up to now. The isolation of the causal characteristics would simplify the transfer of the results to different samples, methods and setups and therefore facilitate the prediction of the occurrence of residual water followed by simplification of the method development. For example the amount of residual water is influenced by kind and amount of SPM at constant experimental conditions. However it is not known on which SPM characteristics the volume of residual water depends. Possible reasons can be the particle size, the pore size or the hydrophilic surface characteristics. The knowledge of the decisive characteristics would be especially helpful for the analysis of the whole water samples with various amounts of SPM and origins as it occurs in monitoring projects and allows the adjustment of the method to different kind of samples. This also applies to the volume flow which also depends on the kind and amount of SPM as well as on the kind of sorbents and its fixation and influences the amount of residual water, too. The dependency on the kind of sorbents and its fixation is also not clarified and can be perhaps reduced to the sorbent particle size and the thickness of the sorbent layer. Furthermore, the clarification of the reasons and the minimisation of the strong fluctuation of the residual water at apparently constant conditions would be helpful due to the influence of residual water on all subsequent analysis steps after the drying process such as elution and instrumental analysis.

Based on the prior results a SPE disk/gas chromatography-mass spectrometry (GC-MS) multi-component trace analysis procedure for the analysis of 1 L whole water sample was developed and validated. The method allows the investigation of surface water containing up to 1000 mg SPM/sample on 54 xenobiotics of different substance groups. Nearly equal high recoveries were determined independent of the presence of SPM in a sample. Compared to liquid-liquid extraction (LLE) and Soxhlet extraction, the developed SPE disk/GC-MS procedure provides higher accuracy and expenditure of time, work, money and the amount of organic solvent could be reduced. In future, besides the expansion of the developed method by other substances and substance groups such as dioxins, alkylphenols and chlorinated paraffins, it is possible to couple the SPE disk sample preparation with other analysis methods such as high performance liquid chromatography.

Part of this study focussed on the improvement of the limits of detection (LODs), since not all required LODs by the Water Framework Directive (WFD) and the German implementation, called Oberflächengewässerverordnung (OGewV), could be achieved by the standard method. Therefore, the SPE disk method was additionally coupled with large volume injection (LVI)/GC-MS to increase sensitivity of the procedure by minimal expenditure. For the first time a SPE disk/LVI/GC-MS method was validated. An improvement of LOQs could be achieved for all 24 analytes, with the exception of only two PAHs. Although LOQs are in the low ng/L level and the LOQs are lower compared to numerous methods described in literature, the requirements of WFD were not achieved for a small number of analytes. A further improvement of LOQs should be easily possible by the extraction of higher sample volumes, e.g. 2 L or more considering the maximal amount of SPM, higher concentration factors and/or higher injection volumes. Admittedly, hardly any study handle large sample volumes, although disk SPE is expressly recommended for large volume samples and consequently experiences with large sample volumes are limited up to now. Another possibility for an improvement of LOQs is the use of more sensitive analytical methods such as GC-MS/MS. In the beginning of 2012, in the regular process of updating the list of priority substances listed in the WFD, further priority substances such as few organic chlorinated pesticides (OCPs), and partly even lower LOQs of already named priority substances as the polychlorinated biphenyls (PCBs) and the polybrominated diphenyl ethers (PBDEs) have been proposed [1] and thus even more sensitive methods are needed, which may require experience with still more sensitive methods such as SPE/LVI/GC-MS/MS.

In general it was shown that disk SPE is a time efficient and suitable sample preparation method for the analysis of the whole water sample for a large number of priority and priority harzardous substances considering the requirements of the WFD by a multi-compound trace analysis.
The combination of SPE disk procedure with both GC-MS methods presented in this study needs only 2.5 h/sample and allows covering of a wide concentration range of analytes and of LOQ values, respectively. The procedure fulfills all requirements of the WFD for 85 % of the 54 investigated analytes (Def. LOQ: S/N = 6:1). Considering the additionally mentioned substances in the German OGewV, still for 74 % of the analytes the demands have been achieved.

In future, besides a further method optimization for example by higher sample volumes and the use of more sensitive analytical methods such as GC-MS/MS as already mentioned above, it will be beneficial to transfer the procedure on a fully automated on-line SPE disk/GC-MS system to save additional work and time and to minimize interferences by manual handling. Currently such a device does not exist for SPE disks with a diameter about 5 cm. Some automated SPE sample preparation systems without coupling to an analytical device are available. The suitability of these systems for the analysis of the whole water sample is partly limited due to plugging of tubes, incomplete sample transfer or sorption effects. Consequently, a further development of on- and offline automated disk SPE sample preparation system seems to be necessary.
In monitoring projects it may be also of interest to extract samples by disk SPE, store it on SPE disks and transport them over wide distances. So far only limited information is available concerning storage of analytes on SPE disks. For example, aspects connected to the whole water sample such as the optimal storage conditions or the practical handling of loose SPM on SPE disks have not yet been considered and in the future may require further attention.

6.1 1.1 References

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7 Supplementary

7.1 General introduction

No supplements.

7.2 Solid-phase extraction disks in water analysis of organic substances

Table 7.1: SPE disk mention in reviews of water analysis

Focus	Titel	Context	Ref.
(I)	The analytical problem of measuring total concentrations of organic pollutants in whole water	Mention of SPE disk	[1]
(I)	Chapter 4 - Sample handling and clean-up procedures II - New developments	Mention SPE disk in a subchapter	[2]
(I)	Recent advances in environmental analysis	Application of SPE disk as passive sampler	[3]
(I)	Multiresidue methods using solid-phase extraction techniques for monitoring priority pesticides, including triazines and degradation products, in ground and surface waters	Design and working of SPE disks	[4]
(I)	Passive samplers for the intergrated chemical and toxicological monitoring of pollutants in ground and surface water (Original title (German): Passivsammler für die zeitintegrierte chemische und toxikologische Überwachung des Schadstoffgehaltes in Grund- und Oberflächenwasser)	Application of SPE disk as passiv sampler	[5]
(I)	Sample preparation	Mention of SPE disk	[6]
(I)	Supercritical fluid chromatography and extraction	Mention of several application of SPE disk	[7]
(I)	Recent developments in polymer-based sorbents for solid-phase extraction	Mention of SPE disk	[8]

Table 7.1: SPE disk mention in reviews of water analysis (continued)

Focus	Titel	Context	Ref.
(I)	Approaches for on-line coupling of extraction and chromatography	Mention of SPE disks	[9]
(I)	Modern methods of sample preparation for GC analysis	Mentioned of SPE disk	[10]
(I)	The application of molecular imprinting technology to solid phase extraction	General information about SPE disks including molecular imprinting of SPE disk	[11]
(I)	Chapter 22 - Sample preparation for water analysis	Mention of SPE disk, however focused on general SPE	[12]
(I)	Fifty years of solid-phase extraction in water analysis - Historical development and overview	Short histrorical overview of SPE disk	[13]
(I)	On-line combination of aqueous-sample preparation and capillary gas chromatography	Mention of SPE disk applications	[14]
(I)	Chapter 32 - New polymeric extraction materials	Mention of SPE disk applications	[15]
(I)	Trace level analysis of micropollutants in aqueous samples using gas chromatography with on-line sample enrichment and large volume injection	Mention of SPE disk	[16]
(I)	Trace enrichment of environmental samples in capillary zone electrophoresis	Mention of SPE disk applications	[17]
(I)	Solid-phase extraction for multiresidue analysis of organic contaminants in water	Mention of SPE disk	[18]
(I)	Trends in extraction of semivolatile compounds from water for environmental analysis	Design and working of SPE disks	[19]
(I)	Organophosphorus flame retardants and plasticizers in water and air II. Analytical methodology	Mention of SPE disk applications	[20]
(I)	Modern extraction techniques	Mention the extistence of SPE disk	[21]
(I)	Automating solid-phase extraction: current aspects and future prospects	Mention of SPE disk of diameter < 5 cm	[22]
(I)	Recent advances in environmental analysis	Mention of SPE disk applications	[23]
(I)	Multiresidue methods using solid-phase extraction techniques for monitoring priority pesticides, including triazines and degradation products, in ground and surface waters	Mentioned of SPE disk	[24]

Table 7.1: SPE disk mention in reviews of water analysis (continued)

Focus	Titel	Context	Ref.
(I)	Extractions with superheated water	Mention of SPE disk	[25]
(I)	Before the injection - Modern methods of sample preparation for separation techniques	Mention of SPE disk applications	[26]
(I)	Advances in solid-phase extraction disks for environmental chemistry	Comprehensive report about SPE disk	[27]
(II)	Preconcentration of contaminants in water analysis	Design and single applications of SPE disks	[28]
(II)	17a-Ethinylestradiol: An endocrine disrupter of great concern. Analytical methods and removal processes applied to water purification. A review	Analysis of EE2 by polystyrene divinylbenzene (SDB) SPE disks	[29]
(II)	Methods for determination of polybrominated diphenyl ethers in environmental samples - Review	Mention SPE disk as passiv sampler	[30]
(II)	Sample treatment in chromatography-based speciation of organometallic pollutants	Mention of SPE disk applications	[31]
(II)	Determination of coal tar and creosote constituents in the aquatic environment	Mention of SPE disk	[32]
(II)	Extraction methodology and chromatography for the determination of residual pesticides in water	Mention of SPE disk applications	[33]
(II)	Trace analysis of pesticides by gas chromatography	Mention of SPE disk	[34]
(II)	Sample preparation for gas chromatographic determination of halogenated volatile organic compounds in environmental and biological samples	Mention SPE disk	[35]
(II)	Analysis of chemicals related to the chemical weapons convention	Single application, use of C_{18} and carbon based SPE disk for analysis of Di-isopropyl methylphosphonate and dimethylphosphonate in contaminated groundwater	[36]
(II)	Comparision of gas and liquid chromatography for analysis polar pesticides in water samples	Mention of SPE disk applications	[37]

Table 7.1: SPE disk mention in reviews of water analysis (continued)

Focus	Titel	Context	Ref.
(II)	Microanalysis of volatile organic compounds (VOCs) in water samples – methods and instruments	Mention SPE disk	[38]
(II)	Modern techniques of extraction of organic analytes from environmental matrices	Mention some possible SPE disk application	[39]
(II)	The analysis of dioxins and related compounds	Mention SPE disk	[40]
(II)	Analytical chemistry of chlorpyrifos and diuron in aquatic ecosystems	Mention SPE disk	[41]
(II)	On-line combination of aqueous-sample preparation and capillary gas chromatography	Mention of SPE disk applications	[42]

(I) Review was focused on a technical part, (II) Review was focused on substance group

Table 7.2: SPE disk method for analysis of organic compounds in water

Reference	[43]	[44]	[45]	[46]
Substance	12 Phenylureas, organophospohorous compounds and triazines	25 Pesticides	11 Pesticides	6 PAH
Matrix	Tap and river water	Distilled, underground, river, lake and sea water	River water	Pure water
Extraction method	SPE	SPE	SPE	Similar SPME
Filtration	Yes (PTFE filter)	Yes (Empore Filter aid)	Yes (PTFE filter)	-
Sorbent	DVB Empore SPE disk	C_{18} Empore SPE disk	C_{18}, DVB (-)	C_{18} ENVI SPE disk
Sample volume	100-1000 mL	1000 mL	2000 mL	150 mL
Enrichment factor	1:100-1:1000	1:1000	1:4000	-
Enrichment speed	20 mL/min	50 mL/min	50 mL/min	-
Drying time	-	-	-	-
Desorption method	Elution	Elution	Elution	-
Analytical method	LC-DAD	GC-FTD, GC-MSD	GC-FTD, GC-MSD	Fluorometric
LOD	0.05-1.0 µg/L	0.05-500 ng/L (FTD), 0.05-15 ng/L (MSD)	2-10 ng/L (C_{18} SPE disk/GC-FTD)	0.01-0.08 µg/L
LOD def.	S/N = 3:1	-	-	Blank + 3 SD
Recovery	23-103 %	33-118 %	78-110 %	-
Comment	On-line method; nine disk system; SPE disk diameter: 4.6 mm	pH_{sample} < 3; modifier: methanol	Monitoring study; pH_{sample} = 2.5; modifier: methanol	-

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[47]	[48]	[49]	[50]
Substance	4 PAH	15 Pesticides	39 phenolic compounds	12 Pesticides
Matrix	Water and urine	Agricultural drainage water	Tap, ground and river water	River, sea and distilled water
Extraction method	Similar SPME	SPE	SPE	SPE
Filtration	-	Yes (glass fibre filter)	Yes (PTFE filter)	Yes (PTFE fiber glass filter)
Sorbent	C_{18} ENVI SPE disk	GCB-4 Empore SPE disk	C_{18}(, C_8) Empore SPE disk	C_{18} Empore SPE disk
Sample volume	150 mL	100-1000 mL	1000 mL	1000-4000 mL
Enrichment factor	-		1:2000	1:10,000
Enrichment speed	-	7-50 mL/min	50 mL/min	8-133 mL/min
Drying time	-		10 min	-
Desorption type	-	(a) Direct analysis, (b) Elution	Elution	Elution
Analytical method	Fluorometric	(a) SALDI-MS, (b) LC-MS/MS	GC-ion-trap/MS	LC-UV/VIS, LC-MS
LOD	0.1-1.2 µg/L	(a) 2-48 µg/L, (b) 4-280 µg/L	2-50 ng/L	2-20 ng/L
LOD def.	-	S/N = 3:1	S/N = 5:1	S/N = 3:1
Recovery %	-	(a) 55-86 %	51-110 %	3-132 %
Comment	-	SPE disk diameter: 13 mm	Derivatization; comparison with LLE and cartridge SPE; pH_{sample} = 11; modifier: Acetic anhydride, NaCl	-

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[51]	[52]	[53]	[54]
Substance	7 Pesticides	8 Dyes	Atrazine, simazine and 2,3,4-trichlorophenol	Carbendazim, chloridazon, simazine and 4-chloroaniline
Matrix	Surface Water	Waste water	Tap water	Milli-Q-water
Extraction method	SPE	SPE	SPE	SPE
Filtration	Yes (glass fibre filter)	Yes (filter paper)	-	-
Sorbent	C_{18} Empore SPEdisk	C_{18} Empore SPE disk	C_{18} Empore SPE disk	C_{18}, SM-2 and AG 50W-X8 Empore SPE disk
Sample volume	1000 mL	250 mL	10 mL	30 mL
Enrichment factor	1:500 mL	1:250	1:5	-
Enrichment speed	20 mL/min	-	2.5 mL/min	2 mL/min
Drying time		-	-	-
Desorption method	Elution, SFE	Elution	Elution	Elution
Analytical method	GC-ECD	FAB-MS, LC-UV	HPLC-UV	LC-DAD
LOD	5-200 ng/L	1-40 mg/L	0.1-1 µg/L	0.1 µg/L
LOD def.	-	-	-	-
Recovery	20-81 %	63-98 %	84-89 %	10-100 %
Comment	$pH_{sample} \leq 2$	-	On-line method: 3 disk system; SPE disk diameter: 4.6 mm: Off-line method; 15 mm; $pH_{sample} = 3$	On-line method; SPE disk diameter: 4.6 mm; up to 10 SPE disk system of different sorbents; $pH_{sample} = 3$; modifier: SDS

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[55]	[56]	[57]	[58]
Substance	10 Perfluorinated chemicals	5 Organophos-phorus pesticide metabolites	Dicamba, 2,4-dichlorophenoxyacetic acid and atrazine	4-Nonylphenol
Matrix	Drinking water (incl. milk, fish, beef, ect.)	Water	Tap, mineral, reservoir water	Distilled, tap, sea and waste water
Extraction method	SPE	SPE	SPE	SPE
Filtration	No	-	Yes (nylon filter)	Yes, partly (-)
Sorbent	Atlantic HLB SPE disk	SAX Empore SPE disk	C_{18} Empore SPE disk	C_{18} Empore SPE disk
Sample volume	500 mL	100 mL	3 mL	500 mL
Enrichment factor	1:500	1:100	-	ca. 1:100
Enrichment speed	70-86 mL/min	-	5 mL/min	-
Drying time	yes	Yes	No	1 min
Desorption method	Elution	Elution	Elution	Elution
Analytical method	UHPLC-MS/MS	GC-FPD	HPLC-UV	HPLC-UV
LOD	0.4-36 ng/L	0.021-0.12 µg/L	13-57 µg/L	-
LOD def.	S/N = 3:1	S/N = 3:1	Blank + 3·SD	-
Recovery	72-98 %	76-96 %	85-112 %	84-96 %
Comment	Off-line method; SPE disk diameter: 47 mm; pH_{sample} = 3.5	Derivatization; pH_{sample} = 6.5-12; SPE disk diameter: 13 mm	On-line method; SPE disk diameter: 8 mm; pH_{sample} = 3	-

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[59]	[60]	[61]	[62]
Substance	57 OCP's, PCB's, PAH's, phthalate esters, organophos-phorus pesti-cides, herbicides, insecticides	19 OCP's	11 Phenolic compounds	13 Pesticides
Matrix	Pure, tap and sea water	Destilled, tap, sea water (and sediment)	Industrial waste, tap and sea water	Drinking water
Extraction method	SPE	SPE	SPE	SPE
Filtration	Yes (naylon and PTFE filter)	Yes, partly (nylon and PTFE filter)	Yes (glass fiber filter)	Yes (-)
Sorbent	C_{18} (-)	C_{18} Empore SPE disk	C_{18} Empore SPE disk	C_{18} Empore SPE disk
Sample volume	500 mL	1000 mL	100 mL	10-1000 mL
Enrichment factor	1:500	1:2000	1:100	-
Enrichment speed	25-33 mL/min	Ca. 33 mL/min	-	2.5-5 mL/min
Drying time	0.5-5 min	5 min	1 min	-
Desorption method	MASE	Elution	MASE	Backflush-elution
Analytical method	(a) GC-ECD (b) GC-MS	GC-MS	LC-UV	LC-UV/VIS; LC-FD
LOD	-	0.01-0.50 µg/L	-	0.005-5 µg/L
LOD def.	-	S/N = 3:1	-	S/N = 3:1
Recovery	45-93 %	50-121 %	35-103 %	9-95 %
Comment	Modifier: NaCl; drying agents: Na_2SO_4	SPE disk diameter: 17 mm; drying agents: Na_2SO_4	Single and double disk system; pH_{sample} = 2; modifier: methanol, Na_2SO_4;	On-line method; ten disk system; SPE disk diameter: 4.6 mm

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[63]	[64]	[65]	[66]
Substance	17 polychlorinated dibenzo-p-dioxins and dibenzofurans	22 Pesticides	12 Non-ionic aliphatic polyethoxylated surfactants	21 organochlorine pesticides
Matrix	River, sea, raw, drinking, tap water and snow	River water	Raw wastewater	Water for human consumption (e.g. tap, spring and well water)
Extraction method	SPE	SPE	SPE	SPE
Filtration	Yes (glass fiber filter)	Yes (PTFE filter)	No	Yes (glass fibre cellulose, nitrate, acetate, PTFE and nylon filter)
Sorbent	C_{18} Empore SPE disk	C_{18}, DVB Empore SPE disk	DVB Empore SPE disk	C_{18} Bakerbond Speedisk SPE disk
Sample volume	20000-40000 mL	200-1000 mL	20 mL	500 mL
Enrichment factor	1:10,000-1:20,000	1:2000-1:10,000	1:20	1:500
Enrichment speed	160-180 mL/min	10 mL/min	-	150 mL/min
Drying time	30 min	5 min	(a) 0 min (b) 3 d at dessicator	30 min
Desorption method	Soxleth-Extraction	Elution	(a) Elution (b) ASE	Elution
Analytical method	GC-HRMS	GC-MS	HPLC-MS	GC-ECD
LOD	0.02-18 pg/L	0.06-0.2 µg/L (V_{sample} = 500 mL)	0.05-4 µg/L	0.13-1.15 ng/L
LOD def.	S/N = 3:1	S/N = 3:1	S/N = 10:1 (LOQ)	-
Recovery	52-94 %	18-110 %	73-108 %	46-105 %
Comment	SPE disk diameter: 90 mm	Modifier: NaCl	-	Drying agent: Na_2SO_4

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[67]	[68]	[69]	[70]
Substance	4 Metals, 3 pesticides and 3 organics	16 PAHs	7 Pyrethroids	Rotenoids and piperonyl butoxide
Matrix	Drinking, treatment plant, river, wells and pond water	Source of drinking water	Deionized, tap and well water	Surface water
Extraction method	SPE	SPE	SPE	SPE
Filtration	Yes	-	Yesy (ashless paper and glass microfiber)	No
Sorbent	C_{18} ENVI SPE disk	C_{18} ENVI SPE disk	C_{18} (-)	C_{18} Empore SPE disk
Sample volume	-	250 mL	200 mL	1000 mL
Enrichment factor	-	1:1000	1:200	1:1000
Enrichment speed	-	-	20 mL/min	-
Drying time	5 min	-	45 min	-
Desorption method	Elution	Elution	Elution	Elution
Analytical method	FAAS, GC-ECD, HPLC-UV, toxicity tests	GC-MS, HPLC-FLD/UV	GC-ECD	GC-MS, HPLC-UV or HPLC-FLD
LOD	-	28-89 µg/L	0.011-0.150 µg/L	0.3-2 µg/L
LOD def.	-	Blank + 3SD	calibration curve	-
Recovery	6-92 %	56-96 %	76- 93 %	87-100 %
Comment	-	Drying agent: Na_2SO_4	pH_{sample} = 4	Off-line method; SPE disk diameter: 47 mm; modifier: methanol, Na_2SO_3; drying agents: Na_2SO_4; $pH_{sample} < 2$

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[71]	[72]	[73]	[74]
Substance	Interferences in the analysis of chlorotriazines	31 carboxylic acids, phenols, triazines, phosphate pesticides, urea and thiooxamindes	117 Organic compounds	15 phenylureas and triazines
Matrix	Sea water	Surface water	Drinking, source and drinking water in any treatment stage	River, ground water and tap water
Extraction method	SPE	SPE	SPE	SPE
Filtration	Yes (glass fibre filter)	Yes (borosilicate microfiber filter)	-	-
Sorbent	C_{18} Empore SPE disk	C_8, C_{18} Empore SPE disk	C_{18} (-)	SAX, C_{18} Empore SPE disk
Sample volume	5000 mL	200-1500 mL	1000 mL	500 mL
Enrichment factor	1:100,000	1:200-1:15,000	1:1000-1:2000	1:5000
Enrichment speed	33 mL/min	-	50-200 mL/min	-
Drying time	-	-	10 min	-
Desorption method	Elution	Ultrasonic supported solid-liquid extraction	Elution	Elution
Analytical method	GC-NPD, GC-MS	GC-MS, GC-FT-IR-MS	GC-MS	(a) GC-MS (b) HPLC-DAD
LOD	0.02-1 ng/L	-	0.03-2.4 µg/L	(a) 0.05 µg/L (b) 0.1 µg/L
LOD def.	S/N = 3:1	-	SD·t	S/N =3:1
Recovery	-	-	20-142 %	31-117 %
Comment	-	Monitoring study; $pH_{sample} < 2$ (partly)	SPE disk diameter: ≥ 47 mm $pH_{sample} < 2$; modifier: Na_2SO_3; drying agents: Na_2SO_4:	Double disk SPE

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[75]	[76]	[77]	[78]
Substance	diuron and 3 of its major metabolites	15 triazines, chloro-acetanilide herbicides, OCPs and PAHs	6 Phenols	Napthalam and 2 degradation products
Matrix	Ground and surface water	Drinking, ground and pure water	Sea water	River water
Extraction method	SPE	SPE	SPE	SPE
Filtration	Yes (nyflon filter)	-	Yes, glass microfiber filter	Yes (GH polypro filter)
Sorbent	C_{18} Empore SPE disk	C_{18} Bakerbond Speedisk SPE disk	DVB, C_{18} Empore SPE disk	C_{18} SPEC SPE disk
Sample volume	100 mL	1000 mL	250 mL	1000 mL
Enrichment factor	1:67	1:1000	1:250	1:1000
Enrichment speed	-	200 mL/min	20-25 mL/min	-
Drying time	10-15 min	-	1 min	2 min (N_2)
Desorption method	Solid-liquid-Extraction	Elution	Elution	Elution
Analytical method	HPLC-UV	GC-MS	LC-ED	GC-MS, HPLC-UV
LOD	0.5-1 µg/L	0.01-0.05 µg/L	0.01-0.04 µg/L	0.23-0.27 µg/L
LOD def.	S/N =3:1	Lowest detectable concentration	-	3 SD
Recovery	77-99 %	75-128 %	14-111 % (C_{18}), 35-108 % (DVB)	94.5 to 100.3 %
Comment	SPE disk diameter: 25 mm	pH_{sample} = 2; modifier: methanol	pH_{sample} = 2; modifier: methanol (partly); double disk system was tested	pH_{sample} = 5-5.2

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[79]	[80]	[81]	[82]
Substance	Diazinon	14 Pesticides and phthalates	6 PAHs	15 PAHs
Matrix	Surface water of rice fields	ground, surface and tap waters	River water	Tap, river and sea water
Extraction method	SPE	SPE	SPE	SPE
Filtration	-	Yes, partly (PTFE filter)		-
Sorbent	C_{18} SPEC SPE disk	C_8, C_{18} Empore SPE disk	C_{18} SPEC SPE disk	DVB Empore SPE disk
Sample volume	750 mL	500-1000 mL	10-1000 mL	50 mL
Enrichment factor	1:750	min. 1:25-1:100	-	-
Enrichment speed	-	Ca. 20 mL/min	Ca. 20 mL/min	2 mL/min
Drying time	2 min (N_2)	Few minutes	15 min (oven) or 100 mL air	-
Desorption method	Elution	Elution	no	Elution
Analytical method	GC-FID, GC-MS	GC-ECD. GC-NPD, LC-DAD	RTP	HPLC-fluorescence
LOD	-	-	20-900 mg/L	0.2-2.0 ng/L
LOD def.	-	-	3*SD/slop	Statistical based
Recovery	-	17-117 %	-	25-98 %
Comment	Next to other methods; pH_{sample} = 7-11; high ionic strength	Modifier: methanol (partly)	SPE disk diameter: 13/38 mm	On-line method; SPE disk diameter: 4 mm; nine-disk system

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[83]	[84]	[85]	[86]
Substance	16 PAHs	11 Pesticides	Domoic acid and 9 isomeres	8 phenolic xenoestrogens
Matrix	Tap and river water	Distilled water	Sea water	Milli-Q-water, tap and drinking water
Extraction method	SPE	SPE	SPE	SPE
Filtration	-	Yes (filter aid)	Yes (Durapore™ Membrane)	Yes (plastic filters)
Sorbent	C_{18}, DVB Empore SPE disk	C_{18} Empore SPE disk	C_{18} Empore SPE disk	C_{18}, DVB, DVB-RPS Empore SPE disks
Sample volume	100 mL	500 mL	75 mL	1000 mL
Enrichment factor	1:100-1:1000	1:500	Ca. 1:20	1:500
Enrichment speed	-	50 mL/min	Ca. 15 mL/min	-
Drying time	Few minutes	-	-	-
Desorption method	Elution	Elution	Elution	Elution
Analytical method	HPLC-FID	GC-FTD, GC-MSD	LC-MS/MS	LC-ED
LOD	0.2-3.7 ng/L	-	20 ng/L	0.10-20 mg/L
LOD def.	S/N =3:1	-	S/N = 3:1	S/N = 10:1
Recovery	13-100 %	57-113 %	92-111 %	75-100 % (DVB-RPS disk)
Comment	Off-line method; SPE disk diameter: 47 mm; modifier: 2-propanol; drying agents: Na_2SO_4	$pH_{sample} < 3$; modifier: humic acids, NaCl, methanol;	$pH_{sample} < 7$	$pH_{sample} = 3.0$

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[87]	[88]	[89]	[90]
Substance	13 nitro- and chlorophenols	42 pesticides	naptalam, N-(1-napththyl)phthalamic acid (NAP) and 3 metabolites	Atrazine and simazine
Matrix	River, tap and HPLC-grade water	Bottle water	river and well water	tap, river and sea water
Extraction method	SPE	SPE	SPE	SPE
Filtration	Yes (nylon filter)	-	Yes (nylon filter)	-
Sorbent	DVB (-)	C_8, C_{18} ENVI SPE disk	C_{18} Empore SPE disk	MWCNTs (-)
Sample volume	10-250 mL	1000 mL	1000 mL	200 mL
Enrichment factor	-	1:1000	1:1000	Ca. 1:4000
Enrichment speed	2 mL/min	50 mL/min	-	-
Drying time	-	0 min	2 min	10 min
Desorption method	Elution	Elution	Elution	Elution
Analytical method	LC-ED	GC-MS, LC-MS/MS	FTIR	GC-MS
LOD	0.01-1.0 µg/L	2-150 µg/L	72-111 µg/L	2.5-5.0 ng/L
LOD def.	-	S/N = 3:1	3·SEE	S/N = 3:1
Recovery	-	65-120 %	97-98 %	87-110 %
Comment	On-line SPE method; SPE disk diameter: 4.6 mm; ten SPE disk system; pH_{sample} = 2; modifier: Na_2SO_3, methanol;	pH_{sample} = 2.5; drying agents: Na_2SO_4	pH_{sample} = 5.1-5.2	pH_{sample} = 3-9

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[91]	[92]	[93]	[94]
Substance	2 Sulfonylureas	Fenitrothion and 3 transformations products	Temephos and 5 degradation products	17 Phenols
Matrix	Water (and soil)	Estuarine water	Water of rice field	HPLC-grade, tap, river water and industrial effluents
Extraction method	SPE	SPE	SPE	SPE
Filtration		Yes (-)	Yes (glass fiber filter)	No
Sorbent	C_{18} Empore SPE disk	C_{18} Empore SPE disk	C_{18} Empore SPE disk	DVB Speedisk SPE disk
Sample volume	1000 mL	1000 mL	1000 mL	50-500 mL
Enrichment factor	1:10,000	1:10,000	1:10,000	1:150-1:200
Enrichment speed	15 mL/min	-	-	100 mL/min
Drying time	30 min	-	-	30 min
Desorption method	Elution	Elution	Elution	Elution
Analytical method	GC-MS	GC-MS	LC-DAD, LC/TSP/MS	LC-ED
LOD	0.1 µg/L	0.03 µg/L (EI) 0.01 µg/L (NCI)	1-2 ng/L	-
LOD def.	-	S/N = 3:1	S/N =3:1	-
Recovery	78-92 %	95-100 %	-	0-143 %
Comment	pH_{sample} = 2; modifier: methanol; drying agents: Na_2SO_4	Photodegradation study	Degradation study	Compared to SPE cartridge method

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[95]	[96]	[97]	[98]
Substance	10 organo-phosphorus pesticides	10 Organo-phosphorus insecticides	96 pesticides	9 pesticides
Matrix	Estuarine water	Distilled, underground, river, lake and sea water	Drinking water	Milli-Q water, drinking, ground and sea water
Extraction method	SPE	SPE	SPE	SPE/Precolumn
Filtration	Yes (-)	Yes (filter aid)	-	Yes (naylon filter)
Sorbent	C_{18} Empore SPE disk	C_{18}, DVB Empore SPE disk	C_{18} Speedisk SPE disk	C_{18} Empore SPE disk
Sample volume	10 mL	1000 mL	500 mL	60 mL
Enrichment factor	1:100	1:1000-1:10,000	1:500	No
Enrichment speed	-	50 mL/min	-	4 mL/min
Drying time	-	-	10 min	-
Desorption method	Elution	Elution	Elution	Back-Flush
Analytical method	GC-NPD, GC-MS	GC-MS, GC/FTD	GC-MS	LC-DAD
LOD	-	0.01-0.07 µg/L (C_{18})	-	0.01-0.2 µg/L
LOD def.	-	S/N = 3:1	-	Blank + 3·SD
Recovery	-	65-104 % (C_{18}), 61-95 % (DVB)	55-146 %	-
Comment	Degradation study	pH_{sample} = 6.1-7.8; modifier: methanol	Off-line method; SPE disk diameter: 50 mm drying agents: Na_2SO_4	On-line method; SPE disk diameter: 4.6 mm; ten disk system; pH_{sample} = 6-7; modifier: NaCl

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[99]	[100]	[101]	[102]
Substance	atrazine, simazine, alachlor, metolachlor and deethylatrazine	6 Haloacetic acids	25 PAHs, pestivides, PCBs,	23 PAHs
Matrix	Estuarine water	Deionized water	Brackish water (incl. SPM, DOM and salt) and reagents water	Natural waters
Extraction method	SPE	SPE	solid phase deposition	SPE
Filtration	Yes (PTFE fiber glass filter)	-	No	Filter aid
Sorbent	C_{18} Empore SPE disk	SAX (-)	C_{18} Empore SPE disk	C_{18} Empore SPE disk
Sample volume	100 mL	50 mL-500 mL	1000 mL	1000 mL
Enrichment factor	1:333	1:50	-	-
Enrichment speed	13-20 mL/min	10 mL/min	6-8 mL/min	-
Drying time	30 min	-	10 min	-
Desorption method	Elution	Elution	supercritical fluid	Elution
Analytical method	GC-NPD	GC-MS	GC-MS	GC-MS
LOD	-	3-20 µg/L	-	7-56 ng/L
LOD def.	-	S/N = 3:1	-	According to EPA
Recovery	90-107 %	8-88 %	80-128 %	48-116 %
Comment	Storage-test; pH_{sample} = 7.8	Derivatization; pH_{sample} = 5; drying agent: Na_2SO_4	Modifier: acetone	Drying agent: Na_2SO_4

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[103]	[104]	[105]	T
Substance	9 Acidic pharma-ceutical and endocrine disrupting compound	9 organophos-phorus pesticides	Dacthal and its mono- and dicarboxylic acid metabolites	Atrazine, alachlor, and α-cypermethrin
Matrix	River water	Water	Ground, deionized water	Wellspring water
Extraction method	SPE	SPE	SPE	SPE
Filtration	Yes (glass fiber filter)	Yes (PTFE fiberglass lilters)	No	Yes (-)
Sorbent	C_{18} ENVI SPE disk, DVB-XC Empore SPE disk	C_{18}, DVB Empore SPE disk	SAX, C_{18}, DVB SPEC SPE disk	C_{18} Empore SPE disk
Sample volume	500 mL	500 mL	100-1000 mL	500 mL
Enrichment factor	1:500	1:1000	1:100-1:1000	1:500
Enrichment speed	50 mL/min	25 mL/min	100 mL/min	-
Drying time	-	-	1 min	10 min
Desorption method	Elution	Elution	Elution	MAE
Analytical method	GC-NCI-MS	LC-ESP/MS	GC-ECD	TLC
LOD	0.1-45 ng/L	Mostly 0.01 µg/L	50 ng/L	-
LOD def.	-	-	S/N = 3:1	-
Recovery	14-115 %	12-98 %	94-86 %,	93-105 %
Comment	pH_{sample} = 3; derivatization; comparison of SPE disk and cartridges	Parallel to C_{18} cartrideges	pH_{sample} = 2; drying agents: Na_2SO_4	pH_{sample} = 2-2.5

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[107]	[108]	[109]	[110]
Substance	Phthalate esters, bisphenol, 4-n-nonylphenol, 4-tert-octylphenol and chlorophenols	4 Estrogens	67 Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and coplanar PCBs	4 Triazines
Matrix	Tap, river and waste water	Scheldt estuary water	Surface water (river or pond water)	River water
Extraction method	MISPE	SPE	SPE	SPE-MISPE
Filtration	Yes	No	Yes (glass fiber filter)	No
Sorbent	C_{18} Empore and ENVI SPE disk	C_{18}XF Speedisk SPE disk	C_{18} Empore SPE disk	C_{18} ENVI SPE disk
Sample volume	1000 mL	2000 mL	1000-18,000 mL	500 mL
Enrichment factor	1:1000	1:80,000	1:20,000-1:900,000	1:500
Enrichment speed	10-100 mL/min	10 mL/min	100 mL/min	-
Drying time	5 min	30 min	Yes	-
Desorption method	Elution	Elution	PLE	Elution
Analytical method	LC-FLD	GC-MS/MS	Gelchromatography/Al-column chromategra-phy/GC-MS	HPLC-UV/VIS
LOD	7-38 ng/L	0.25 ng/L	-	-
LOD def.	3 SD	Lowest calibration point	-	-
Recovery	59-99 %	102-108 %	70-117 %	86–91 %
Comment	Double disk system	pH_{sample} = 7	pH_{sample} = 2 or 9; SPE disk diameter: 90 mm	Recovery only for SPE

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[111]	[112]	[113]	[114]
Substance	Alachlor	Endosulfan	20 Pesticides	6 Fluorescent whitening agents
Matrix	Milli-Q-water	Water	Surface/river, drinking water	Raw sewage, primary effluent, secondary effluent, and river water
Extraction method	SPE	SPE	SPE	SPE
Filtration	-		No	Yes (glass fiber filter)
Sorbent	C_{18} Empore SPE disk	C_{18} Empore SPE disk	DVB-, C_{18}-Speedisk	C_{18} Empore SPE disk
Sample volume	25-300 mL	25-800 mL	1000 mL	10-200 mL
Enrichment factor	1:25-1:30,000	1:25-1:500	1:5000	1:10-1:200
Enrichment speed	Ca. 30 mL/min	-	200 mL/min	-
Drying time	30 min	30 min	Few second	2 min
Desorption method	Elution	Elution	Elution	Elution
Analytical method	GC-ECD, GC-MS	GC-ECD, GC-MS	HPLC-DAD	HPLC-UV-FD
LOD	-	-	0.01-0.05 µg/L (drinking water)	0.2-0.3 ng/L
LOD def.	-	-	S/N = 3:1	S/N = 10:1
Recovery	-	39-88 %	25-100 % (pH = 6)	76-96 %
Comment	Degradation study	Degradation and storing study	Modifier: methanol	SPE disk diameter: 25 mm

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[115]	[116]	[117]
Substance	25 Phenoles, nitroaromatics, nitroalkane, alcohols, chlorphenols, ect.	Atrazine and 3 metabolites	18 Chlorinated phenols and phenols
Matrix	Water	Ground water	Ground water
Extraction method	SPE	SPE	SPE
Filtration	-	-	Yes (-)
Sorbent	DVB Empore SPE disk	C_{18} ENVI SPE disk	C_{18}, DVB Empore SPE disk
Sample volume	0-1000	1000 mL	1000 mL
Enrichment factor	Max. 1:40	20mL	1:1000
Enrichment speed	40-60 mL/min	20 mL/min	-
Drying time	1 min	24 h at room temperature	-
Desorption method	Elution	SFE	Backflush-elution
Analytical method	GC-FID	GC-NPD	LC-UV
LOD	-	0.3-0.7 ng/L	0.1-4 µg/L
LOD def.	-	Blank+3SD	-
Recovery	-	19-100 %	20-86 %
Comment	Determination of break through volume	Modifier: NaCl, methanol	Manuel method compared to on-line method; pH_{sample} = 2.0

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[118]	[119]	[120]
Substance	17 Polychlorinated dibenzo-p-dioxins and dibenzofurans	Thiobencarb	13 Organochlorine compounds
Matrix	Waste, deionized, rain, sea water, industrial effluent, landfill leachate	Water (and soil) from a rice field	Milli-Q, laboratory and lake water
Extraction method	SPE	SPE	SPE
Filtration	Yes for Empores SPE disk (filter aid, cellulose filter, glass wool, sand)	Yes (-)	Yes (glass fiber filter)
Sorbent	C_{18} Empore SPE disk, C_{18} Speedisk SPE disk	C_{18} Empore SPE disk	C_8, C_{18} Empore SPE disk and C_{18} SPEC SPE disk
Sample volume	2000-10,000 mL	1000 mL	500 mL
Enrichment factor	1:133,333-1:666,666	1:1000	1:500
Enrichment speed	-	-	40 mL/min
Drying time	Yes	-	0.5 min + 2h in Exiccation
Desorption method	Elution	Elution	Elution
Analytical method	GC-MS	GC-NPD	GC-ECD
LOD	0.3-11 pg/L (Empore SPE disk), 0.1-4 pg/L (Speedisk SPE disk)	34 ng/L (water)	-
LOD def.	S/N = 3:1	Blank+3SD	-
Recovery	78-109 %	93 %	48-82 %
Comment	pH_{sample} = 5-6; modifier: methanol	-	Off-line method; SPE disk diameter: 47 mm; pH_{sample} = 3; drying agent: Na_2SO_4

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[121]	[122]	[123]	[124]
Substance	10 Phenyl urea herbicides	4 Biocides	Sea-Nine 211 and 8 transformation products	16 Phenols
Matrix	Laboratory and river water	Sea water	Sea, river, lake and distilled water	Distilled, tap and river water
Extraction method	SPE	SPE	SPE	MISPE
Filtration	-	-	No	-
Sorbent	C_{18} Empore SPE disk	C_{18} Empore SPE disk	DVB Empore SPE disk	DVB Empore SPE disk
Sample volume	1000 mL	500 mL	50-700 mL	200-500 mL
Enrichment factor	1:1000	1:5000	1:500-1:7000	1:20-1:50
Enrichment speed	-	-	2.5-20 mL/min	200 mL/min
Drying time	-	-	10 min	-
Desorption method	Elution,	Elution	Elution	Elution
Analytical method	HPLC-DAD, Photolysis/Deri-vatization/HPLC-DAD partly	GC-MSD, GC-ECD, GC-FTD	GC-ECD, GC-MS	HPLC-UV, GC-FID
LOD	4-50 ng/L	0.42-9.5 ng/L	-	-
LOD def.	SD·t	-	-	-
Recovery	94-121 %	56-93 %	-	73-100 %
Comment	Off-line method; SPE disk diameter: 47 mm; pH_{sample} = 2; modifier: Na_2SO_3, methanol	pH_{sample} < 3; modifier: methanol;	Photodegradation study; modifier: methanol; drying agent: Na_2SO_4;	pH_{sample} = 2; modifier: NaCl

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[125]	[126]	[127]	[128]
Substance	43 Phenolic pesticides	12 Pesticides	12 Pesticides	12 Pesticides
Matrix	Milli-Q-water	Deionized water	Deionized water	Deionized water
Extraction method	SPE	SPE	SPE	SPE
Filtration	-	-	-	Yes (glass microfiber filters)
Sorbent	C_{18}, DVB Empore SPE disk	C_{18} Empore SPE disk	C_{18} Empore SPE disk	C_{18} Empore SPE disk
Sample volume	1000 mL	250 mL	250 mL	250 mL
Enrichment factor	1:500	1:50	1:50	1:125
Enrichment speed	30 mL/min	25-30 mL/min	25-30 mL/min	25-30 mL/min
Drying time	-	5 min	5 min	5 min
Desorption method	Elution	Elution	Elution	Elution
Analytical method	HPLC-UV	GC-MS	GC-ECD, HPLC-UV	GC-MS
LOD	6-300 ng/L	-	-	-
LOD def.	S/N = 6:1	-	-	-
Recovery	38-124 %	37-106 %	0-114 %	34-101
Comment	Comparison between SPE disk and cartridges; modifier: methanol	Storing study; $pH_{sample} \approx 5$; modifier: methanol; drying agent: Na_2SO_4, $CaSO_4$, freez-drying, desiccation	Storing study; modifier: methanol; drying agent: Na_2SO_4	Invetigation of humic acid and Ca-Montmorillinite; pH_{sample} = 6-8; modifier: KH_2PO_4/NaOH buffer; drying agent: Na_2SO_4

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[129]	[130]	[131]	[132]
Substance	17 Pesticides	17 Pesticides	4 pesticides	6 Estrogens
Matrix	Surface water	Ground water	Surface and deionized water	Waste, surface and nanopure water
Extraction method	SPE	SPE	SPE	SPE
Filtration	Yes (paper filter)	-	Yes (glass fiber filter and nylon membrane filter)	Yes (glass fiber filters)
Sorbent	- Empore SPE disk	- Empore SPE disk	C_{18} Empore SPE disk	DVB-XC Empore SPE disk
Sample volume	250 mL	250 mL	1000 mL	Up to 5000 mL
Enrichment factor	1:50	1:50	1:200	Up to 1:2500
Enrichment speed	25-30 mL/min	25-30 mL/min	-	-
Drying time	5 min	5 min	5 min	-
Desorption method	Elution	Elution	Liquid-solid extraction	Elution
Analytical method	GC-ECD, HPLC-UV	GC-ECD, HPLC-UV	GC-MS, GC-NPD, GC-ECD, GC-FID	HPLC-DAD, HPLC-RIA
LOD	0.1-1.0 µg/L	0.1-1.0 µg/L	0.1-0.5 µg/L	9-208 µg/L
LOD def.	S/N = 3:1	S/N = 3:1	-	10 SD
Recovery	72-98 %	82-98 %	14-112 %	46-78 %
Comment	Monitoring study; drying agent: Na_2SO_4	Monitoring study; modifier: methanol; drying agent: Na_2SO_4	Interlabor study; modifier: methanol; drying agent: Na_2SO_4	SPE disk diameter: 90 mm; drying agent: Na_2SO_4;

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[133]	[134]	[135]	[136]
Substance	5 Pesticides	12 Polar pesticides and their transformation	9 Alkylphosphonic acids	2 Methylphos-phonothiolate
Matrix	River, estuarine and marine water	Surface, estuarine and sea water	Water	Milli-Q, river and bay water
Extraction method	SPE	SPE	SPE	SPE
Filtration	Yes (GF/C fiber glass filter, Durapore filter)	Yes (ME-25 filter)	-	-
Sorbent	DVB Empore SPE disk	GCB Empore SPE disk	SAX Empore SPE disk	SAX Empore SPE disk
Sample volume	200 -1000 mL	1000 mL	5 mL	0.5-5 mL
Enrichment factor	1:1000-1:5000	1:5000	1:100	1:100
Enrichment speed	40 mL/min	-	1 mL/min	1 mL/min
Drying time	45 min	-	15 min	15 min
Desorption method	Elution	Backflush-elution	Liquid-solid extraction	Liquid-solid extraction
Analytical method	LVI/GC-MS	LC-ESI-MS/MS	GC-MS	GC-MS
LOD	0.2-5.0 ng/L (V_{sample} = 200 mL)	0.1-8.0 ng/L	0.14 µg/L	10 µg/L (SIM), 100 µg/L (scan)
LOD def.	S/N = 3:1	S/N = 3:1	S/N = 3:1	S/N = 3:1
Recovery	70-104 %	9-80 %	83-101 %	87-104 %
Comment	-	pH_{sample} = 7	SPE disk diameter: 13 mm	SPE disk diameter: 13 mm

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[137]	[138]	[139]	[140]
Substance	15 Androgens	15 steroidal oral contraceptives	39 Chlorophenols, chlorocatechols and chloroguaiacols	3 Fluorescent whitening agents
Matrix	Influent of a waste water treatment plant and effluent of a fish farm	Tap, river, lake and waste water	Milli-Q-water	Lake water
Extraction method	SPE	SPE	SPE or static extraction	SPE
Filtration	Yes (nylon filter)	Yes (nylon filter)	-	No
Sorbent	C_8, C_{18} ENVI SPE disk	C_8, C_{18} ENVI SPE disk	C_{18}, AC Empore SPE disk	C_{18} Empore SPE disk
Sample volume	200 mL	100-1000 mL	100-400 mL	200 mL
Enrichment factor	1:1000	1:1000-1:10,000	1:100-1:400	1:400
Enrichment speed	50-150 mL/min	50-150 mL/min	50 mL/min for SPE	-
Drying time	Yes	5 min	20 min	5 min
Desorption method	Elution	Elution	Dynamic/Elution or static desorption	Elution
Analytical method	LC-MS/MS	UPLC–MS/MS	GC-MS	HPLC/UV
LOD	0.5-4 ng/L	0.5-3.4 ng/L	-	0.2-3 ng/L
LOD def.	S/N = 3:1	-	-	10·SD
Recovery	78-108 %	76-102 %	10-124 %	87-95 %
Comment	-	-	Derivatization	SPE disk diameter: 25 mm

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[141]	[142]	[143]	[144]
Substance	10 Phthalic acid monoesters	Diquat and paraquat	15 Polychlorinated dibenzo-p-dioxins and poly-chlorinated dibenzofurans	13 Herbicides
Matrix	River water	Drinking water	Industrial effluent and surface water	Drinking water
Extraction method	SPE	SPE	SPE	SPE
Filtration	Yes, partly (glass filter)	-	Yes (filter aid, sand particle retention paper, glass wool)	-
Sorbent	DVB-XD Empore SPE disk	C_8 ENVI SPE disk	C_{18} Empore SPE disk	C_{18} Empore SPE disk
Sample volume	250-500 mL	500 mL	1000 mL	1000 mL
Enrichment factor	1:1000	1:400	1:1000	1:1000
Enrichment speed	50-100 mL/min	-	-	50 mL/min
Drying time	5 min	-	5 min	1 min
Desorption method	Elution	Elution	Elution	Elution
Analytical method	GC-MS	LC-MS	GC-MS/MS, GC-HRMS	GC-MS
LOD	2-30 ng/L	0.10-0.2 µg/L	-	2-9 ng/L
LOD def.	SD·t	[145]	-	SD·t
Recovery	59-105 %	-	89 %	51-140 %
Comment	Derivatization; pH_{sample} = 2; cartridges were also tested; drying agent: Na_2SO_4	Modifier: methanol	SPE disk diameter: 47/90 mm; pH_{sample} = 3; modifier: methanol; drying agent: Na_2SO_4	Derivatization; pH_{sample} = 2 or 7; modifier: methanol

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Reference	[146]	[147]	[148]	[149]
Substance	N-Nitrosodi-methylamine	9 Polar pesticides	18 pesticides	7 Triazinic herbicides
Matrix	Drinking and ground water	Milli-Q water	Distilled water, marsh water	Milli-Q, mineral, natural well and tap water
Extraction method	SPE	Passive sampling	SPE	SPE
Filtration	-	-	Yes (filter aid)	Yes (nylon filter)
Sorbent	C_{18} + carbon disk Empore SPE disk	DVB-XC, -RPS Empore SPE disk	C_{18} SPEC SPE disk	C_{18}, DVB Empore SPE disk
Sample volume	1000 mL	5000 mL	10,000 mL	1000 mL
Enrichment factor	1:5000	1:5000	1:10,000	1:1000
Enrichment speed	40-50 mL/min	0.004 m/s, 3-21 d	130-150 mL/min	-
Drying time	10 min	1 min	1 min	Yes
Desorption method	Elution	Elution, (ultra-sonic extraction)	Elution	Elution
Analytical method	GC-CLND	HPLC-UV	GC-MS	MEKC-DAD
LOD	2 ng/L	-	0.05-2 ng/L	20-300 ng/L
LOD def.	SD·t	-	-	S/N = 3:1
Recovery	57 %	21-98 %	31-117 %	71-104 %
Comment	Double disk system	pH_{sample} = 3.7	SPE disk diameter: 90/47 mm; water and SPM analysed separately; modi-fier: methanol; drying agent: Na_2SO_4	Double disk system; pH_{sample} = 12

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Ref.	[150]	[151]	[152]	[153]
Substance	16 PAH	4 Pesticides	Diquat and Paraquat	44 Pesticides
Matrix	Sea water	Surface and sea water (and sediments)	Spring and tap water	Distilled water
Extraction method	SPE	SPE	SPE	SPE
Filtration	-	Yes (filter aid)	Yes (glass fiber filter)	-
Sorbent	DVB Empore SPE disk	SDS(, C_{18}) Empore SPE disk	C_{18} (-)	C_8, C_{18} Empore SPE disk
Sample volume	4000 mL	1000 mL	10 mL	500 mL
Enrichment factor	1:4000	1:5000	-	1:2500
Enrichment speed	-	35 mL/min	-	-
Drying time	-	10 min	2-3 min	-
Desorption method	Solid-liquid extraction	Backflush elution	Direct analysis	Elution
Analytical method	GC-MS	GC-ECD, GC-MS	MALDI	GC-ECD, GC-NPD
LOD	-	1-15 ng/L	0.32-0.64 µg/L	-
LOD def.	-	S/N = 3:1	S/N = 3:1	-
Recovery	-	75-97 %	-	37-97%
Comment	SPE disk diameter: 90 mm; $pH_{sample} < 7$	SPM: sonication and subsequent SPE; $pH_{sample} = 3$; drying argent: Na_2SO_4	SPE disk diameter: < 47 mm	Modifier: methan-ol; comparison between disk and cartridge

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Ref.	[154]	[155]	[156]	[157]
Substance	17 Nitroaromatic, nitramine, nitrate-ester explosives and contaminants	16 PAH	7 PCB	Sum of anionic surfactants
Matrix	reagent-grade and ground water	Surface water	Reagent, ground water	River and sewage water
Extraction method	SPE	SPE	SPE	SPE+LLE
Filtration	-	No	Yes (glass microfibre filters)	Yes
Sorbent	DVB Empore SPE disk	C_{18} Speedisk SPE disk	C_{18} SPEC, ENVI and Empore SPE disk	C_{18} Empore SPE disk
Sample volume	50-1000 mL	1000 mL	1000 mL	500 mL
Enrichment factor	1:10-1:250	1:200-1:1000	1:500	1:33
Enrichment speed	-	50 mL/min	-	21-36 mL/min
Drying time	15-20 min	7 min	10 min	Yes
Desorption method	Elution	Elution	Elution	Elution
Analytical method	GC-ECD	GC-MS	GC-ECD	UV
LOD	0.04-0.4 µg/L	1-5 ng/L	-	-
LOD def.	SD (n=7)	S/N = 4:1	-	-
Recovery	74-116 %	58-106 %	91–107 %	95-101 %
Comment	Also Sep-PakVac PorapakRDX cartridges were used	Off-line method; SPE disk diameter: 50 mm	Drying agent: Florisil, Na_2SO_4	Modifier: methan-ol; $pH_{sample} < 7$

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

Ref.	[158]	[159]	[160]
Substance	6 Crown ethers	10 PCB	9 Pesticides
Matrix	Water	Waste water	Water
Extraction method	SPE	SPE	Dynamic extraction
Filtration	-	Yes (3 glass microfiber filters)	-
Sorbent	C_{18} Empore SPE disk	C_{18} Empore SPE disk	C_{18} Empore SPE disk
Sample volume	500 mL	1000 mL	800 mL
Enrichment factor	1:250	1:500	-
Enrichment speed	23-50 mL/min	1.5 mL/min	-
Drying time	5 min	15 min+ 24 h in a desicator	-
Desorption method	Elution	SFE	Static extraction
Analytical method	GC-FID	GC-ECD	GC-MS
LOD	70-290 µg/L	ca. 0.1-0.2 µg/L	-
LOD def.	-	S/N = 3:1	-
Recovery	0-104 %	56-177 %	5-90 %
Comment	pH_{sample} = 6.8	-	-

Table 7.2: SPE disk method for analysis of organic compounds in water (continued)

-: no information available, ASE: accelerated solvent extraction, CLND: chemiluminescent nitrogen detector, DAD: diode area detector, ECD: electron capture detector, ED: Multi-electrode electrochemical detector, ESP: high-flow pneumatically assisted electrospray, FAAS: flame atomic absorption spectrometry, FAB: fast atom bombardment, FD: fluorescence detection, FID: flame ionisation detector, FLD: flourescence detector, FTD: flame thermionic detector, FT-IR-MS: Fourier transform infrared mass spectrometer, GC: gas chromatography, GCB: graphitized carbon black, HLB: hydrophilic/lipophilic balanced, HPLC: high performance liquid chromatography, HRMS: high resolution mass spectrometry, LC: liquid chromatography, LLE: liquid-liquid extraction, LOD: limit of detection, LVI: large volume injection, MAE: Microwave-assisted extraction, MALDI: matrix-assisted laser desorption/ionization, MEKC: micellar electrokinetic chromatography, MISPE: molecularly imprinted solid-phase extraction, MS: mass spectrometry, MSD: mass selective detector, MWCNT: multi wall carbon nano tubes, NPD: nitrogene phosphorus detector, OCP: organo chloro pesticides, PAH: polycyclic aromatic hydrocarbons, PCB: Polychlorinated biphenyl, pH_{sample}: pH value of the sample, PLE: Pressurized liquid extraction, PTFE: polytetrafluoroethylene, RIA: radioimmunoassay, RTP: room-temperature phosphorimetry, SALDI: surface-assisted laser desorption ionization mass spectrometry, SAX: strong anion exchange, SD: standard deviation, SFE: supercritical fluid extraction, DVB: styrene divinylbenzene, DVB-RPS: Sulfonated DVB material, SDS: Sodium dodecyl sulphate, SEE: Standard error estimation ~ SD, S/N: signal to noise ratio, SPED: solid phase derivatization, SPE: solid phase extraction, SPME: solid phase micro extraction, SALDI: surface-assisted laser desorption/ionization, t: student'st value, TLC: thin layer chromatography, UHPLC: ultra high performance liquid chromatography, UV: ultra violet detector, VIS: visible, V_{sample}: sample volume

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7.3 Occurrence of residual water within disk-based solid-phase extraction and its effect on GC-MS measurement of organic extracts of environmental samples

Redrafted from "C. Erger, P. Balsaa, F. Werres, T.C. Schmidt, Occurrence of residual water within disk-based solid-phase extraction and its effect on GC-MS measurement of organic extracts of environmental samples, Anal. Bioanal. Chem. 403 (2012) 254", DOI 10.1007/s00216-011-5659-y,

7.3.1 Drying

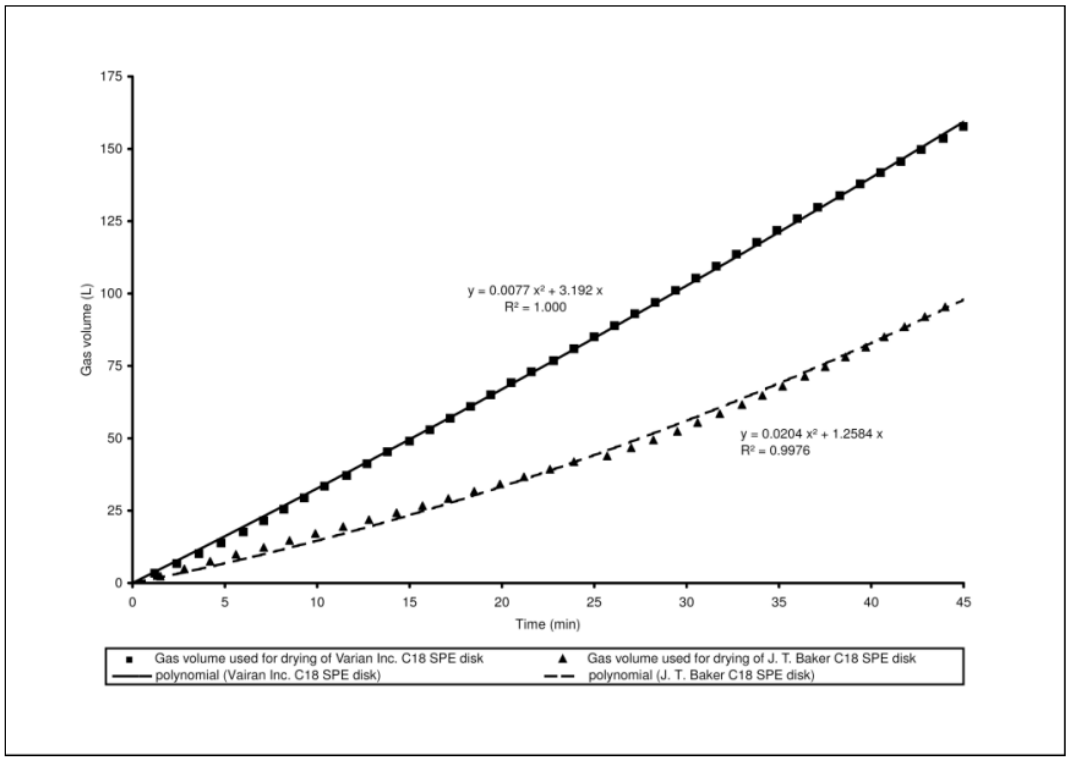

Figure 7.1: Total gas volume depending on the drying time for C_{18} SPE disks of both J. T. Baker and Varian Inc.

Table 7.3: Recoveries after different drying times using Bakerbond Speedisk Extraction Disk C_{18} and acetone (3 x 3 mL; contact time: 1 min, 5 min, 1 min) as eluent (n = 3)

Substances	7 min drying time	60 min drying time
1,3,5-Trichlorobenzene	81 ± 3 %	64 ± 3 %
1,2,4-Trichlorobenzene	87 ± 4 %	76 ± 3 %
Naphthalene	101 ± 4 %	88 ± 1 %
Hexachlorobutadiene	54 ± 1 %	48 ± 4 %
1,2,3-Trichlorobenzene	83 ± 5 %	76 ± 4 %
3,4-Dichlorobenzene	95 ± 3 %	89 ± 3 %
Acenaphthylene	93 ± 5 %	88 ± 2 %
Acenaphthene-D_{10}	92 ± 3 %	88 ± 3 %
Acenaphthene	95 ± 4 %	90 ± 4 %
Pentachlorobenzene	81 ± 3 %	76 ± 6 %
Fluorene	93 ± 5 %	93 ± 4 %
Trifluralin	88 ± 3 %	79 ± 3 %
4,4'-Dibromooctafluorobiphenyl	75 ± 3 %	73 ± 4 %
alpha-HCH	97 ± 1 %	100 ± 3 %
Hexachlorobenzene	76 ± 2 %	70 ± 5 %
Simazine	78 ± 2 %	77 ± 4 %
Atrazine-D_5	64 ± 5 %	93 ± 2 %
Atrazine	80 ± 1 %	99 ± 4 %
beta-HCH	91 ± 6 %	98 ± 3 %
gamma-HCH	94 ± 4 %	94 ± 3 %
Phenanthrene	94 ± 5 %	98 ± 3 %
Anthracene-D_{10}	84 ± 2 %	89 ± 4 %
Anthracene	81 ± 3 %	86 ± 1 %
delta-HCH	104 ± 4 %	110 ± 3 %
4-n-Nonylphenol-D_8	61 ± 3 %	63 ± 6 %
PCB 28	79 ± 3 %	78 ± 7 %
Alachlor	92 ± 4 %	95 ± 2 %
PCB 52	78 ± 2 %	77 ± 5 %
Chlorpyriphos-ethyl	93 ± 1 %	105 ± 5 %
Aldrin	84 ± 8 %	78 ± 2 %
Isodrin	96 ± 4 %	96 ± 5 %
Chlorfenvinphos	91 ± 3 %	95 ± 4 %
Fluoranthene	82 ± 2 %	89 ± 2 %
PCB 101	74 ± 2 %	66 ± 2 %
Pyrene	84 ± 2 %	87 ± 3 %
alpha-Endosulfan	109 ± 7 %	90 ± 5 %
p,p'-DDE	73 ± 2 %	64 ± 1 %

Table 7.3: Recovery after different drying times using Bakerbond Speedisk Extraction Disk C_{18} and acetone (3 x 3 mL; contact time: 1 min, 5 min, 1 min) as eluent (n = 3) (continued)

Substances	7 min drying time	60 min drying time
Dieldrin	106 ± 1 %	86 ± 4 %
Endrin	80 ± 2 %	90 ± 1 %
beta-Endosulfan	77 ± 1 %	77 ± 5 %
p,p'-TDE	73 ± 1 %	76 ± 5 %
o,p'-DDT	88 ± 8 %	79 ± 3 %
PCB 153	57 ± 0 %	52 ± 4 %
p,p'-DDT	80 ± 1 %	82 ± 6 %
PCB 138	57 ± 2 %	50 ± 4 %
Benzo[a]anthracene	74 ± 3 %	79 ± 6 %
Chrysene-D_{12}	68 ± 3 %	69 ± 1 %
Chrysene	69 ± 3 %	82 ± 3 %
PCB 180	50 ± 2 %	48 ± 3 %
Benzo[b]fluoranthene	71 ± 4 %	68 ± 6 %
Benzo[k]fluoranthene	64 ± 5 %	64 ± 2 %
Benzo[a]pyrene	60 ± 2 %	58 ± 2 %
Indeno[1,2,3-c,d]pyrene	55 ± 1 %	51 ± 3 %
Dibenzo[a,h]anthracene	49 ± 3 %	47 ± 4 %
Benzo[g,h,i]perylene	51 ± 2 %	48 ± 3 %

7.4 Multi-component trace analysis of organic xenobiotics in surface water containing suspended particular matter by solid phase extraction/gas chromatography-mass spectrometry

Redrafted from "C. Erger, P. Balsaa, F. Werres, T.C. Schmidt, Multi-component trace analysis of organic xenobiotics in surface water containing suspended particular matter by solid phase extraction/gas chromatography-mass spectrometry, J. Chromatogr., A 1249 (2012) 181", DOI 10.1016/j.chroma.2012.06.018,

7.4.1 Solutions

Table 7.4: Preparation of the used stock solution by weighing and solving the standards in a defined volume of solvent and the concentration of the purchased solutions

Name	Solvent	Substance	Weight mg	Volume mL	Concentration mg/L
PAH - mix by EPA, 100 mg/L	Acetonitrile	Acenaphthene			100
		Acenaphthylene			100
		Anthracene			100
		Benz[a]anthracene			100
		Benzo[a]pyrene			100
		Benzo[b]fluoranthene			100
		Benzo[g,h,i]perylene			100
		Benzo[k]fluoranthene			100
		Chrysene			100
		Dibenzo[a,h]anthracene			100
		Fluoranthene			100
		Fluorene			100
		Indeno[1,2,3-c,d]pyrene			100
		Naphthalene			100
		Phenanthrene			100
		Pyrene			100
Alachlor, 400 mg/L	Ethyl acetate	Alachlor	20.0	50	400
Aldrin, 402 mg/L	Ethyl acetate	Aldrin	20.1	50	402
Atrazine, 392 mg/L	Ethyl acetate	Atrazine	19.6	50	392

Table 7.4: Preparation of the used stock solution by weighing and solving the standards in a defined volume of solvent and the concentration of the purchased solutions (continued)

Name	Solvent	Substance	Weight mg	Volume mL	Concentration mg/L
Chlorfenvinphos, 440 mg/L	Ethyl acetate	Chlorfenvinphos	11.0		440
Chlorpyrifos-ethyl, 396 mg/L	Ethyl acetate	Chlorpyrifos-ethyl	9.9		396
p,p'-DDE, 392 mg/L	Ethyl acetate	p,p'-DDE	19.6	50	392
p,p'-TDE, 426 mg/L	Ethyl acetate	p,p'-TDE	21.3	50	426
p,p'-DDT, 392 mg/L	Ethyl acetate	p,p'-DDT	19.6	50	392
o,p'-DDT, 408 mg/L	Ethyl acetate	o,p'-DDT	20.4	50	408
Dieldrin, 390 mg/L	Ethyl acetate	Dieldrin	19.5	50	390
alpha-Endosulfan, 408 mg/L	Ethyl acetate	alpha-Endosulfan	20.4	50	408
beta-Endosulfan, 456 mg/L	Ethyl acetate	beta-Endosulfan	22.8	50	456
Endrin, 416 mg/L	Ethyl acetate	Endrin	20.8	50	416
Hexachlorobenzene, 412 mg/L	Ethyl acetate	Hexachlorobenzene	20.6	50	412
Hexachlorobutadiene, 436 mg/L	Ethyl acetate	Hexachlorobutadiene	21.0	50	420
alpha-HCH, 388 mg/L	Ethyl acetate	alpha-HCH	19.4	50	388
beta-HCH, 386 mg/L	Ethyl acetate	beta-HCH	19.3	50	386
gamma-HCH, 436 mg/L	Ethyl acetate	gamma-HCH	21.8	50	436
delta-HCH, 416 mg/L	Ethyl acetate	delta-HCH	20.8	50	416
Isodrin, 396 mg/L	Ethyl acetate	Isodrin	19.8	50	396
Pentachlorobenzene, 394 mg/L	Ethyl acetate	Pentachlorobenzene	19.7	50	394
Simazine, 408 mg/L	Ethyl acetate	Simazine	20.4	50	408
1,2,3-Trichlorobenzene, 400 mg/L	Ethyl acetate	1,2,3-Trichlorobenzene	20.0	50	400
1,2,4-Trichlorobenzene, 440 mg/L	Ethyl acetate	1,2,4-Trichlorobenzene	22.0	50	440
1,3,5-Trichlorobenzene, 380 mg/L	Ethyl acetate	1,3,5-Trichlorobenzene	19.0	50	380
Trifluralin, 396 mg/L	Ethyl acetate	Trifluralin	19.8	50	396

Table 7.4: Preparation of the used stock solution by weighing and solving the standards in a defined volume of solvent and the concentration of the purchased solutions (continued)

Name	Solvent	Substance	Weight mg	Volume mL	Concentration mg/L
PCB Mix 1, 10 mg/L	Acetonitrile	PCB 28			10
		PCB 52			10
		PCB 101			10
		PCB 138			10
		PCB 153			10
		PCB 180			10
BDE 28, 50 mg/L	Nonane				50
BDE 47, 50 mg/L	Nonane				50
BDE 99, 50 mg/L	Nonane				50
BDE 100, 50 mg/L	Nonane				50
BDE 153, 50 mg/L	Nonane				50
BDE 154, 50 mg/L	Nonane				50
PAK (IS), 210 mg/L	Acetone	Chrysene-D_{12} (IS)	2.1	10	210
		Acenaphthene-D_{10} (IS)	2.1	10	210
		Anthracene-D_{10} (IS)	2.1	10	210
3,4-Dichloronitrobenzene, 560 mg/L (IS)	Acetone	3,4-Dichloronitrobenzene (IS)	5.6	10	560
4,4'-Dibromooctafluoro-biphenyl (IS), 250 mg/L	Acetone	4,4'-Dibromooctafluoro-biphenyl (IS)			250
Atrazine-D_5 (IS), 100 mg/L	Acetonitrile	Atrazine-D_5 (IS)	5	50	100
Fluoranthene-D_{10} (VS), 210 mg/L	Acetone	Fluoranthene-D_{10} (VS)	2.1	10	210
PCB 208 (VS), 100 mg/L	Hexane	PCB 208			100

Table 7.5: Preparation of the diluted standard solution and the used volumetric standard by diluting of defined volume in acetone

Name	Solution	Volume mL	Flask size mL	Final concentration mg/L
PAH - mix, 10 mg/L	PAH - mix by EPA, 100 mg/L	0.100	1	10.0
PAH - mix, 1 mg/L	PAH - mix by EPA, 100 mg/L	0.100	10	1.0
PSM - mix, 10 mg/L	Alachlor, 400 mg/L	0.500	20	10.0
	Aldrin, 402 mg/L	0.500		10.1
	Atrazine, 392 mg/L	0.500		9.8
	Chlorfenvinphos, 440 mg/L	0.500		11.0
	Chlorpyrifos-ethyl, 396 mg/L	0.500		9.9
	p,p'-DDE, 392 mg/L	0.500		9.8
	p,p'-TDE, 426 mg/L	0.500		10.7
	p,p'-DDT, 392 mg/L	0.500		9.8
	o,p'-DDT, 408 mg/L	0.500		10.2
	Dieldrin, 390 mg/L	0.500		9.8
	alpha-Endosulfan, 408 mg/L	0.500		10.2
	beta-Endosulfan, 456 mg/L	0.500		11.4
	Endrin, 416 mg/L	0.500		10.4
	Hexachlorobenzene, 412 mg/L	0.500		10.3
	Hexachlorobutadiene, 436 mg/L	0.500		10.5
	alpha-HCH, 388 mg/L	0.500		9.7
	beta-HCH, 386 mg/L	0.500		9.7
	gamma-HCH, 436 mg/L	0.500		10.9
	delta-HCH, 416 mg/L	0.500		10.4
	Isodrin, 396 mg/L	0.500		9.9
	Pentachlorobenzene, 394 mg/L	0.500		9.9
	Simazine, 408 mg/L	0.500		10.2
	1,2,3-Trichlorobenzene, 400 mg/L	0.500		10.0
	1,2,4-Trichlorobenzene, 440 mg/L	0.500		11.0
	1,3,5-Trichlorobenzene, 380 mg/L	0.500		9.5
	Trifluralin, 396 mg/L	0.500		9.9
PSM - mix, 1 mg/L	PSM - mix, 10 mg/L	1.000	10	1.0
PCB - mix, 1 mg/L	PCB Mix 1, 10 mg/L	0.100	1	1.0

Table 7.5: Preparation of the diluted standard solution and the used volumetric standard by diluting of defined volume in acetone (continued)

Name	Solution	Volume	Flask size	Final concentration
		mL	mL	mg/L
BDE - mix, 1 mg/L	BDE 28, 50 mg/L	0.100	5	1.0
	BDE 47, 50 mg/L	0.100		
	BDE 99, 50 mg/L	0.100		
	BDE 100, 50 mg/L	0.100		
	BDE 153, 50 mg/L	0.100		
	BDE 154, 50 mg/L	0.100		
PAK (IS), 10 mg/L	PAK (IS), 210 mg/L	0.500	10	10.5
4,4'-Dibromooctafluoro-biphenyl (IS), 50 mg/L	4,4'-Dibromooctafluorobiphenyl (IS), 250 mg/L	0.200	1	50.0
Fluoranthene-D_{10} (VS), 10 mg/L	Fluoranthene-D_{10} (VS), 210 mg/L	0.050	1	10.5
Volumetric standard (VS), 10 mg/L	Fluoranthene-D_{10} (VS), 210 mg/L	0.050	1	10.5
	PCB 208 (VS), 100 mg/L	0.100		10.0
Fluoranthene-D_{10}, 250 µg/L (VS)	Fluoranthene-D_{10} (VS), 10 mg/L	0.250	10	0.263

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Internal standard (IS)	PAK (IS), 10 mg/L	0.120	Chrysene-D_{12} (IS)	0.126	25.2
			Acenaphthene-D_{10} (IS)	0.126	25.2
			Anthracene-D_{10} (IS)	0.126	25.2
	3,4-Dichloronitrobenzene (IS), 560 mg/L	0.050	3,4-Dichloronitrobenzene (IS)	2.800	560.0
	4,4'-Dibromooctafluoro-biphenyl (IS), 50 mg/L	0.050	4,4'-Dibromoocta-fluorobiphenyl (IS)	0.250	50.0
	Atrazine-D_5 (IS), 100 mg/L	0.200	Atrazine-D_5 (IS)	2.000	400.0
Spike I	PAH - mix, 1 mg/L	0.250	Acenaphthene	0.025	5.0
			Acenaphthylene	0.025	5.0
			Anthracene	0.025	5.0
			Benz[a]anthracene	0.025	5.0
			Benzo[a]pyrene	0.025	5.0
			Benzo[b]fluoranthene	0.025	5.0
			Benzo[g,h,i]perylene	0.025	5.0
			Benzo[k]fluoranthene	0.025	5.0
			Chrysene	0.025	5.0
			Dibenzo[a,h]anthracene	0.025	5.0
			Fluoranthene	0.025	5.0
			Fluorene	0.025	5.0
			Indeno[1,2,3-c,d]pyrene	0.025	5.0
			Naphthalene	0.025	5.0
			Phenanthrene	0.025	5.0
			Pyrene	0.025	5.0

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike I (continued)	PSM - mix, 1 mg/L	0.250	Alachlor	0.025	5.0
			Aldrin	0.025	5.0
			Atrazine	0.025	4.9
			Chlorfenvinphos	0.028	5.5
			Chlorpyrifos-ethyl	0.025	5.0
			p,p'-DDE	0.025	4.9
			p,p'-TDE	0.027	5.3
			p,p'-DDT	0.025	4.9
			o,p'-DDT	0.026	5.1
			Dieldrin	0.024	4.9
			alpha-Endosulfan	0.026	5.1
			beta-Endosulfan	0.029	5.7
			Endrin	0.026	5.2
			Hexachlorobenzene	0.026	5.2
			Hexachlorobutadiene	0.027	5.5
			alpha-HCH	0.024	4.9
			beta-HCH	0.024	4.8
			gamma-HCH	0.027	5.5
			delta-HCH	0.026	5.2
			Isodrin	0.025	5.0
			Pentachlorobenzene	0.025	4.9
			Simazine	0.026	5.1
			1,2,3-Trichlorobenzene	0.025	5.0
			1,2,4-Trichlorobenzene	0.028	5.5
			1,3,5-Trichlorobenzene	0.024	4.8
			Trifluralin	0.025	5.0
	PCB - mix, 1 mg/L	0.250	PCB 28	0.025	5.0
			PCB 52	0.025	5.0
			PCB 101	0.025	5.0
			PCB 138	0.025	5.0
			PCB 153	0.025	5.0
			PCB 180	0.025	5.0

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike I (continued)	BDE - mix, 1 mg/L	0.250	BDE 28	0.025	5.0
			BDE 47	0.025	5.0
			BDE 99	0.025	5.0
			BDE 100	0.025	5.0
			BDE 153	0.025	5.0
			BDE 154	0.025	5.0
	PAK (IS), 10 mg/L	0.120	Chrysene-D_{12} (IS)	0.126	25.2
			Acenaphthene-D_{10} (IS)	0.126	25.2
			Anthracene-D_{10} (IS)	0.126	25.2
	3,4-Dichloronitrobenzene (IS), 560 mg/L	0.050	3,4-Dichloro-nitrobenzene (IS)	2.800	560.0
	4,4'-Dibromooctafluoro-biphenyl (IS), 50 mg/L	0.050	4,4'-Dibromoocta-fluorobiphenyl (IS)	0.250	50.0
	Atrazine-D_5 (IS), 100 mg/L	0.200	Atrazine-D_5 (IS)	2.000	400.0
Spike II	PAH - mix, 1 mg/L	0.625	Acenaphthene	0.063	12.5
			Acenaphthylene	0.063	12.5
			Anthracene	0.063	12.5
			Benz[a]anthracene	0.063	12.5
			Benzo[a]pyrene	0.063	12.5
			Benzo[b]fluoranthene	0.063	12.5
			Benzo[g,h,i]perylene	0.063	12.5
			Benzo[k]fluoranthene	0.063	12.5
			Chrysene	0.063	12.5
			Dibenzo[a,h]anthracene	0.063	12.5
			Fluoranthene	0.063	12.5
			Fluorene	0.063	12.5
			Indeno[1,2,3-c,d]pyrene	0.063	12.5
			Naphthalene	0.063	12.5
			Phenanthrene	0.063	12.5
			Pyrene	0.063	12.5

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike II (continued)	PSM - mix, 1 mg/L	0.625	Alachlor	0.063	12.5
			Aldrin	0.063	12.6
			Atrazine	0.061	12.3
			Chlorfenvinphos	0.069	13.8
			Chlorpyrifos-ethyl	0.062	12.4
			p,p'-DDE	0.061	12.3
			p,p'-TDE	0.067	13.3
			p,p'-DDT	0.061	12.3
			o,p'-DDT	0.064	12.8
			Dieldrin	0.061	12.2
			alpha-Endosulfan	0.064	12.8
			beta-Endosulfan	0.071	14.3
			Endrin	0.065	13.0
			Hexachlorobenzene	0.064	12.9
			Hexachlorobutadiene	0.068	13.6
			alpha-HCH	0.061	12.1
			beta-HCH	0.060	12.1
			gamma-HCH	0.068	13.6
			delta-HCH	0.065	13.0
			Isodrin	0.062	12.4
			Pentachlorobenzene	0.062	12.3
			Simazine	0.064	12.8
			1,2,3-Trichlorobenzene	0.063	12.5
			1,2,4-Trichlorobenzene	0.069	13.8
			1,3,5-Trichlorobenzene	0.059	11.9
			Trifluralin	0.062	12.4
	PCB - mix, 1 mg/L	0.625	PCB 28	0.063	12.5
			PCB 52	0.063	12.5
			PCB 101	0.063	12.5
			PCB 138	0.063	12.5
			PCB 153	0.063	12.5
			PCB 180	0.063	12.5

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike II (continued)	BDE - mix, 1 mg/L	0.625	BDE 28	0.063	12.5
			BDE 47	0.063	12.5
			BDE 99	0.063	12.5
			BDE 100	0.063	12.5
			BDE 153	0.063	12.5
			BDE 154	0.063	12.5
	PAK (IS), 10 mg/L	0.120	Chrysene-D_{12} (IS)	0.126	25.2
			Acenaphthene-D_{10} (IS)	0.126	25.2
			Anthracene-D_{10} (IS)	0.126	25.2
	3,4-Dichloronitrobenzene (IS), 560 mg/L	0.050	3,4-Dichloro-nitrobenzene (IS)	2.800	560.0
	4,4'-Dibromooctafluoro-biphenyl (IS), 50 mg/L	0.050	4,4'-Dibromoocta-fluorobiphenyl (IS)	0.250	50.0
	Atrazine-D_5 (IS), 100 mg/L	0.200	Atrazine-D_5 (IS)	2.00	400.0
Spike III	PAH - mix, 1 mg/L	1.000	Acenaphthene	0.100	20.0
			Acenaphthylene	0.100	20.0
			Anthracene	0.100	20.0
			Benz[a]anthracene	0.100	20.0
			Benzo[a]pyrene	0.100	20.0
			Benzo[b]fluoranthene	0.100	20.0
			Benzo[g,h,i]perylene	0.100	20.0
			Benzo[k]fluoranthene	0.100	20.0
			Chrysene	0.100	20.0
			Dibenzo[a,h]anthracene	0.100	20.0
			Fluoranthene	0.100	20.0
			Fluorene	0.100	20.0
			Indeno[1,2,3-c,d]pyrene	0.100	20.0
			Naphthalene	0.100	20.0
			Phenanthrene	0.100	20.0
			Pyrene	0.100	20.0

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike III (continued)	PSM - mix, 1 mg/L	1.000	Alachlor	0.100	20.0
			Aldrin	0.101	20.1
			Atrazine	0.098	19.6
			Chlorfenvinphos	0.110	22.0
			Chlorpyrifos-ethyl	0.099	19.8
			p,p'-DDE	0.098	19.6
			p,p'-TDE	0.107	21.3
			p,p'-DDT	0.098	19.6
			o,p'-DDT	0.102	20.4
			Dieldrin	0.098	19.5
			alpha-Endosulfan	0.102	20.4
			beta-Endosulfan	0.114	22.8
			Endrin	0.104	20.8
			Hexachlorobenzene	0.103	20.6
			Hexachlorobutadiene	0.109	21.8
			alpha-HCH	0.097	19.4
			beta-HCH	0.097	19.3
			gamma-HCH	0.109	21.8
			delta-HCH	0.104	20.8
			Isodrin	0.099	19.8
			Pentachlorobenzene	0.099	19.7
			Simazine	0.102	20.4
			1,2,3-Trichlorobenzene	0.100	20.0
			1,2,4-Trichlorobenzene	0.110	22.0
			1,3,5-Trichlorobenzene	0.095	19.0
			Trifluralin	0.099	19.8
	PCB - mix, 1 mg/L	1.000	PCB 28	0.100	20.0
			PCB 52	0.100	20.0
			PCB 101	0.100	20.0
			PCB 138	0.100	20.0
			PCB 153	0.100	20.0
			PCB 180	0.100	20.0

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike III (continued)	BDE - mix, 1 mg/L	1.000	BDE 28	0.100	20.0
			BDE 47	0.100	20.0
			BDE 99	0.100	20.0
			BDE 100	0.100	20.0
			BDE 153	0.100	20.0
			BDE 154	0.100	20.0
	PAK (IS), 10 mg/L	0.120	Chrysene-D_{12} (IS)	0.126	25.2
			Acenaphthene-D_{10} (IS)	0.126	25.2
			Anthracene-D_{10} (IS)	0.126	25.2
	3,4-Dichloronitrobenzene (IS), 560 mg/L	0.050	3,4-Dichloro-nitrobenzene (IS)	2.800	560.0
	4,4'-Dibromooctafluoro-biphenyl (IS), 50 mg/L	0.050	4,4'-Dibromoocta-fluorobiphenyl (IS)	0.250	50.0
	Atrazine-D_5 (IS), 100 mg/L	0.200	Atrazine-D_5 (IS)	2.000	400.0
Spike IV	PAH - mix, 10 mg/L	0.135	Acenaphthene	0.135	27.0
			Acenaphthylene	0.135	27.0
			Anthracene	0.135	27.0
			Benz[a]anthracene	0.135	27.0
			Benzo[a]pyrene	0.135	27.0
			Benzo[b]fluoranthene	0.135	27.0
			Benzo[g,h,i]perylene	0.135	27.0
			Benzo[k]fluoranthene	0.135	27.0
			Chrysene	0.135	27.0
			Dibenzo[a,h]anthracene	0.135	27.0
			Fluoranthene	0.135	27.0
			Fluorene	0.135	27.0
			Indeno[1,2,3-c,d]pyrene	0.135	27.0
			Naphthalene	0.135	27.0
			Phenanthrene	0.135	27.0
			Pyrene	0.135	27.0

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike IV (continued)	PSM - mix, 10 mg/L	0.135	Alachlor	0.135	27.0
			Aldrin	0.136	27.1
			Atrazine	0.132	26.5
			Chlorfenvinphos	0.149	29.7
			Chlorpyrifos-ethyl	0.134	26.7
			p,p'-DDE	0.132	26.5
			p,p'-TDE	0.144	28.8
			p,p'-DDT	0.132	26.5
			o,p'-DDT	0.138	27.5
			Dieldrin	0.132	26.3
			alpha-Endosulfan	0.138	27.5
			beta-Endosulfan	0.154	30.8
			Endrin	0.140	28.1
			Hexachlorobenzene	0.139	27.8
			Hexachlorobutadiene	0.147	29.4
			alpha-HCH	0.131	26.2
			beta-HCH	0.130	26.1
			gamma-HCH	0.147	29.4
			delta-HCH	0.140	28.1
			Isodrin	0.134	26.7
			Pentachlorobenzene	0.133	26.6
			Simazine	0.138	27.5
			1,2,3-Trichlorobenzene	0.135	27.0
			1,2,4-Trichlorobenzene	0.149	29.7
			1,3,5-Trichlorobenzene	0.128	25.7
			Trifluralin	0.134	26.7
	PCB - mix, 10 mg/L	0.135	PCB 28	0.135	27.0
			PCB 52	0.135	27.0
			PCB 101	0.135	27.0
			PCB 138	0.135	27.0
			PCB 153	0.135	27.0
			PCB 180	0.135	27.0

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike IV (continued)	BDE - mix, 1 mg/L	1.350	BDE 28	0.135	27.0
			BDE 47	0.135	27.0
			BDE 99	0.135	27.0
			BDE 100	0.135	27.0
			BDE 153	0.135	27.0
			BDE 154	0.135	27.0
	PAK (IS), 10 mg/L	0.120	Chrysene-D_{12} (IS)	0.126	25.2
			Acenaphthene-D_{10} (IS)	0.126	25.2
			Anthracene-D_{10} (IS)	0.126	25.2
	3,4-Dichloronitrobenzene (IS), 560 mg/L	0.050	3,4-Dichloro-nitrobenzene (IS)	2.800	560.0
	4,4'-Dibromooctafluoro-biphenyl (IS), 50 mg/L	0.050	4,4'-Dibromoocta-fluorobiphenyl (IS)	0.250	50.0
	Atrazine-D_5 (IS), 100 mg/L	0.200	Atrazine-D_5 (IS)	2.000	400.0
Spike V	PAH - mix, 10 mg/L	0.175	Acenaphthene	0.175	35.0
			Acenaphthylene	0.175	35.0
			Anthracene	0.175	35.0
			Benz[a]anthracene	0.175	35.0
			Benzo[a]pyrene	0.175	35.0
			Benzo[b]fluoranthene	0.175	35.0
			Benzo[g,h,i]perylene	0.175	35.0
			Benzo[k]fluoranthene	0.175	35.0
			Chrysene	0.175	35.0
			Dibenzo[a,h]anthracene	0.175	35.0
			Fluoranthene	0.175	35.0
			Fluorene	0.175	35.0
			Indeno[1,2,3-c,d]pyrene	0.175	35.0
			Naphthalene	0.175	35.0
			Phenanthrene	0.175	35.0
			Pyrene	0.175	35.0

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike V (continued)	PSM - mix, 10 mg/L	0.175	Alachlor	0.175	35.0
			Aldrin	0.176	35.2
			Atrazine	0.172	34.3
			Chlorfenvinphos	0.193	38.5
			Chlorpyrifos-ethyl	0.173	34.7
			p,p'-DDE	0.172	34.3
			p,p'-TDE	0.186	37.3
			p,p'-DDT	0.172	34.3
			o,p'-DDT	0.179	35.7
			Dieldrin	0.171	34.1
			alpha-Endosulfan	0.179	35.7
			beta-Endosulfan	0.200	39.9
			Endrin	0.182	36.4
			Hexachlorobenzene	0.180	36.1
			Hexachlorobutadiene	0.191	38.2
			alpha-HCH	0.170	34.0
			beta-HCH	0.169	33.8
			gamma-HCH	0.191	38.2
			delta-HCH	0.182	36.4
			Isodrin	0.173	34.7
			Pentachlorobenzene	0.172	34.5
			Simazine	0.179	35.7
			1,2,3-Trichlorobenzene	0.175	35.0
			1,2,4-Trichlorobenzene	0.193	38.5
			1,3,5-Trichlorobenzene	0.166	33.3
			Trifluralin	0.173	34.7
	PCB - mix, 10 mg/L	0.175	PCB 28	0.175	35.0
			PCB 52	0.175	35.0
			PCB 101	0.175	35.0
			PCB 138	0.175	35.0
			PCB 153	0.175	35.0
			PCB 180	0.175	35.0

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike V (continued)	BDE - mix, 1 mg/L	1.750	BDE 28	0.175	35.0
			BDE 47	0.175	35.0
			BDE 99	0.175	35.0
			BDE 100	0.175	35.0
			BDE 153	0.175	35.0
			BDE 154	0.175	35.0
	PAK (IS), 10 mg/L	0.120	Chrysene-D_{12} (IS)	0.126	25.2
			Acenaphthene-D_{10} (IS)	0.126	25.2
			Anthracene-D_{10} (IS)	0.126	25.2
	3,4-Dichloronitrobenzene (IS), 560 mg/L	0.050	3,4-Dichloro-nitrobenzene (IS)	2.800	560.0
	4,4'-Dibromooctafluoro-biphenyl (IS), 50 mg/L	0.050	4,4'-Dibromoocta-fluorobiphenyl (IS)	0.250	50.0
	Atrazine-D_5 (IS), 100 mg/L	0.200	Atrazine-D_5 (IS)	2.000	400.0
Spike VI	PAH - mix, 10 mg/L	0.210	Acenaphthene	0.210	42.0
			Acenaphthylene	0.210	42.0
			Anthracene	0.210	42.0
			Benz[a]anthracene	0.210	42.0
			Benzo[a]pyrene	0.210	42.0
			Benzo[b]fluoranthene	0.210	42.0
			Benzo[g,h,i]perylene	0.210	42.0
			Benzo[k]fluoranthene	0.210	42.0
			Chrysene	0.210	42.0
			Dibenzo[a,h]anthracene	0.210	42.0
			Fluoranthene	0.210	42.0
			Fluorene	0.210	42.0
			Indeno[1,2,3-c,d]pyrene	0.210	42.0
			Naphthalene	0.210	42.0
			Phenanthrene	0.210	42.0
			Pyrene	0.210	42.0

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike VI (continued)	PSM - mix, 10 mg/L	0.210	Alachlor	0.210	42.0
			Aldrin	0.211	42.2
			Atrazine	0.206	41.2
			Chlorfenvinphos	0.231	46.2
			Chlorpyrifos-ethyl	0.208	41.6
			p,p'-DDE	0.206	41.2
			p,p'-TDE	0.224	44.7
			p,p'-DDT	0.206	41.2
			o,p'-DDT	0.214	42.8
			Dieldrin	0.205	41.0
			alpha-Endosulfan	0.214	42.8
			beta-Endosulfan	0.239	47.9
			Endrin	0.218	43.7
			Hexachlorobenzene	0.216	43.3
			Hexachlorobutadiene	0.229	45.8
			alpha-HCH	0.204	40.7
			beta-HCH	0.203	40.5
			gamma-HCH	0.229	45.8
			delta-HCH	0.218	43.7
			Isodrin	0.208	41.6
			Pentachlorobenzene	0.207	41.4
			Simazine	0.214	42.8
			1,2,3-Trichlorobenzene	0.210	42.0
			1,2,4-Trichlorobenzene	0.231	46.2
			1,3,5-Trichlorobenzene	0.200	39.9
			Trifluralin	0.208	41.6
	PCB - mix, 10 mg/L	0.210	PCB 28	0.210	42.0
			PCB 52	0.210	42.0
			PCB 101	0.210	42.0
			PCB 138	0.210	42.0
			PCB 153	0.210	42.0
			PCB 180	0.210	42.0

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike VI (continued)	BDE - mix, 1 mg/L	2.100	BDE 28	0.210	42.0
			BDE 47	0.210	42.0
			BDE 99	0.210	42.0
			BDE 100	0.210	42.0
			BDE 153	0.210	42.0
			BDE 154	0.210	42.0
	PAK (IS), 10 mg/L	0.120	Chrysene-D_{12} (IS)	0.126	25.2
			Acenaphthene-D_{10} (IS)	0.126	25.2
			Anthracene-D_{10} (IS)	0.126	25.2
	3,4-Dichloronitrobenzene (IS), 560 mg/L	0.050	3,4-Dichloro-nitrobenzene (IS)	2.800	560.0
	4,4'-Dibromooctafluoro-biphenyl (IS), 50 mg/L	0.050	4,4'-Dibromoocta-fluorobiphenyl (IS)	0.250	50.0
	Atrazine-D_5 (IS), 100 mg/L	0.200	Atrazine-D_5 (IS)	2.000	400.0
Spike VII	PAH - mix, 10 mg/L	0.250	Acenaphthene	0.250	50.0
			Acenaphthylene	0.250	50.0
			Anthracene	0.250	50.0
			Benz[a]anthracene	0.250	50.0
			Benzo[a]pyrene	0.250	50.0
			Benzo[b]fluoranthene	0.250	50.0
			Benzo[g,h,i]perylene	0.250	50.0
			Benzo[k]fluoranthene	0.250	50.0
			Chrysene	0.250	50.0
			Dibenzo[a,h]anthracene	0.250	50.0
			Fluoranthene	0.250	50.0
			Fluorene	0.250	50.0
			Indeno[1,2,3-c,d]pyrene	0.250	50.0
			Naphthalene	0.250	50.0
			Phenanthrene	0.250	50.0
			Pyrene	0.250	50.0

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike VII (continued)	PSM - mix, 10 mg/L	0.250	Alachlor	0.250	50.0
			Aldrin	0.251	50.3
			Atrazine	0.245	49.0
			Chlorfenvinphos	0.275	55.0
			Chlorpyrifos-ethyl	0.248	49.5
			p,p'-DDE	0.245	49.0
			p,p'-TDE	0.266	53.3
			p,p'-DDT	0.245	49.0
			o,p'-DDT	0.255	51.0
			Dieldrin	0.244	48.8
			alpha-Endosulfan	0.255	51.0
			beta-Endosulfan	0.285	57.0
			Endrin	0.260	52.0
			Hexachlorobenzene	0.258	51.5
			Hexachlorobutadiene	0.273	54.5
			alpha-HCH	0.243	48.5
			beta-HCH	0.241	48.3
			gamma-HCH	0.273	54.5
			delta-HCH	0.260	52.0
			Isodrin	0.248	49.5
			Pentachlorobenzene	0.246	49.3
			Simazine	0.255	51.0
			1,2,3-Trichlorobenzene	0.250	50.0
			1,2,4-Trichlorobenzene	0.275	55.0
			1,3,5-Trichlorobenzene	0.238	47.5
			Trifluralin	0.248	49.5
	PCB - mix, 10 mg/L	0.250	PCB 28	0.250	50.0
			PCB 52	0.250	50.0
			PCB 101	0.250	50.0
			PCB 138	0.250	50.0
			PCB 153	0.250	50.0
			PCB 180	0.250	50.0

Table 7.6: Preparation of the eight used spike solutions for the method calibration in the concentration range from 0 to 50 ng/L of the target compounds in the sample; solvent: acetone; flask size: 10 mL; spike volume: 200 µL; sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Concentration spike solution mg/L	Concentration sample ng/L
Spike VII (continued)	BDE - mix, 1 mg/L	2.500	BDE 28	0.250	50.0
			BDE 47	0.250	50.0
			BDE 99	0.250	50.0
			BDE 100	0.250	50.0
			BDE 153	0.250	50.0
			BDE 154	0.250	50.0
	PAK (IS), 10 mg/L	0.120	Chrysene-D_{12} (IS)	0.126	25.2
			Acenaphthene-D_{10} (IS)	0.126	25.2
			Anthracene-D_{10} (IS)	0.126	25.2
	3,4-Dichloronitrobenzene (IS), 560 mg/L	0.050	3,4-Dichloronitro-benzene (IS)	2.800	560.0
	4,4'-Dibromooctafluoro-biphenyl (IS), 50 mg/L	0.050	4,4'-Dibromoocta-fluorobiphenyl (IS)	0.250	50.0
	Atrazine-D_5 (IS), 100 mg/L	0.200	Atrazine-D_5 (IS)	2.000	400.0

7.4.2 Chromatograms

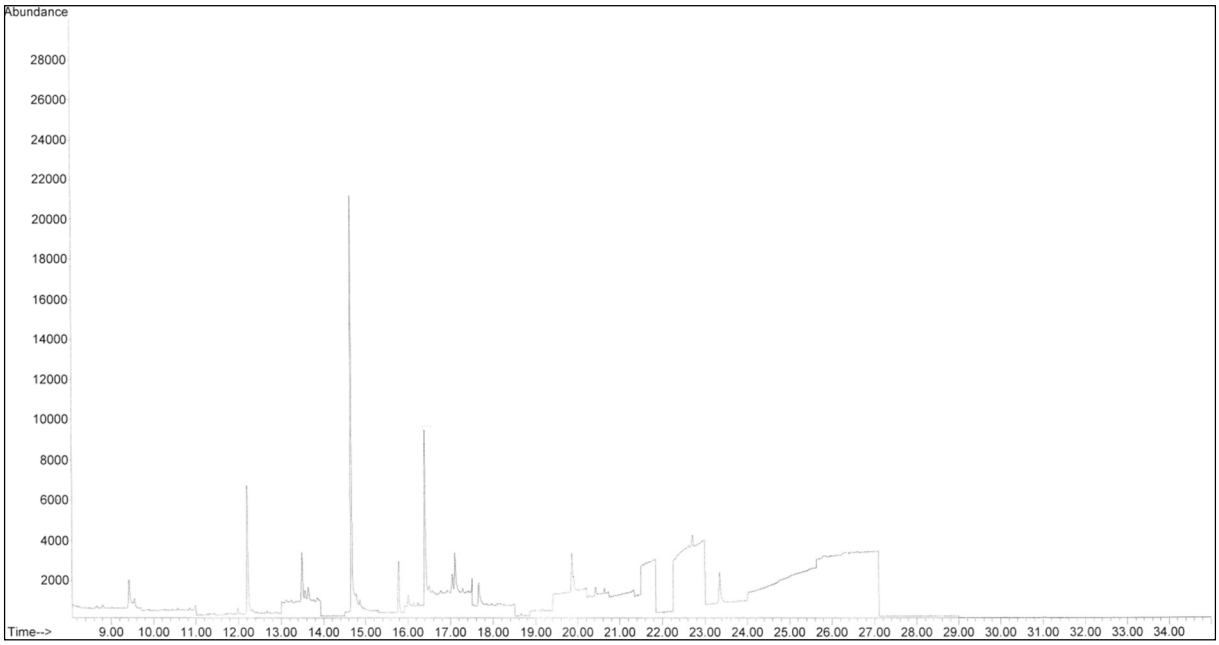

Figure 7.2: Total ion current chromatogram in selected ion monitoring mode of filtered water of river Ruhr used as matrix for the method validation

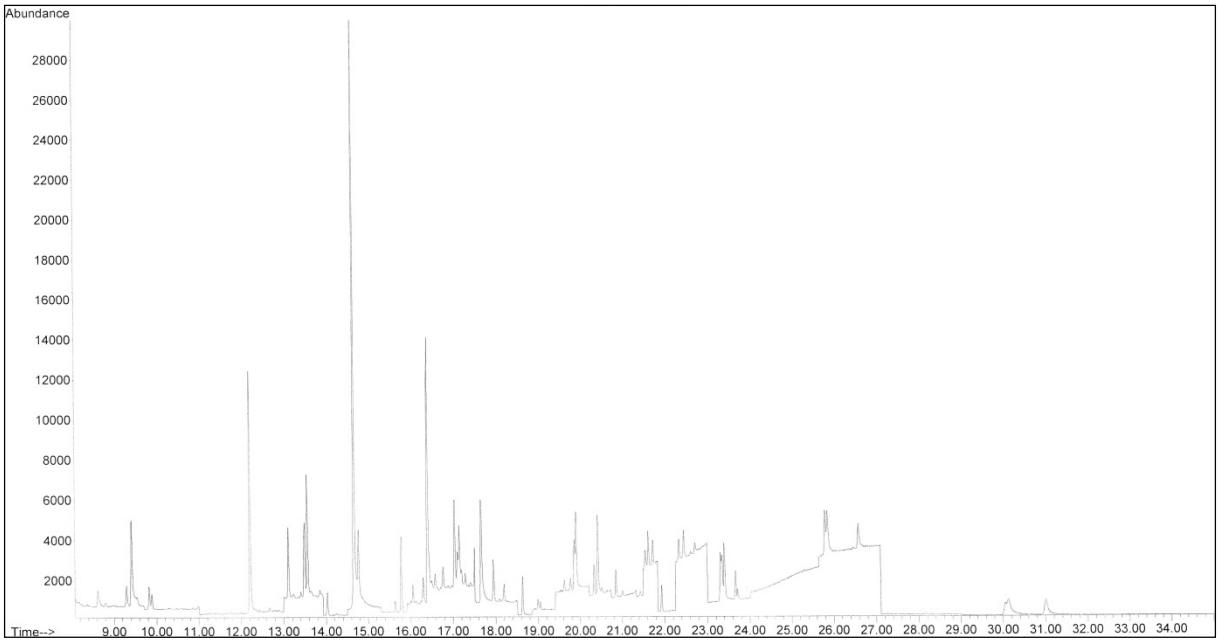

Figure 7.3: Total ion current chromatogram in selected ion monitoring mode of filtered water of river Ruhr spiked with ca. 27 ng/L analyte (Spike IV, Tab. S 3)

7.4.3 Recoveries and limits of quantification (LOQ) without concentration step

Table 7.7: Recovery in surface water spiked with analytes (27.5 ng/L), sediment (PAH-Loamy Clay 1, 250 mg) or analytes and sediment (27.5 ng/L analytes + PAH-Loamy Clay 1, 250 mg); n = 5, without consideration of the concentration step by evaporation of the extraction solvent

	Recovery analytes	Recovery sediment	Recovery analytes and sediment	Certified reference value for sediment
	%	%	%	ng/g
1,3,5-Trichlorobenzene	50 ± 13	n.d.	62 ± 17	-
1,2,4-Trichlorobenzene	67 ± 6	n.d.	78 ± 23	-
Naphthalene	72 ± 6	94 ± 18	100 ± 25	464 ± 118
Hexachlorobutadiene	55 ± 8	n.d.	55 ± 14	-
1,2,3-Trichlorobenzene	76 ± 5	n.d.	77 ± 20	-
3,4-Dichloronitrobenzene	54 ± 10	50 ± 23	66 ± 16	-
Acenaphthylene	69 ± 6	111± 18	99 ± 26	53.4 ± 31.9
Acenaphthene-D_{10} (IS)	80 ± 2	82 ± 17	87 ± 24	-
Acenaphthene	88 ± 6	≤ LOQ	82 ± 23	29.9 ± 19.0
Pentachlorobenzene	71 ± 8	n.d.	64 ± 18	-
Fluorene	110 ± 11	≤ LOQ	27 ± 7	408 ± 125
Trifluralin	87 ± 5	n.d.	93 ± 11	-

Table 7.8: Limits of quantification (LOQ) and AA-EQS for inland waters of the WFD without consideration of the concentration step by evaporation of the extraction solvent

	LOQ S/N = 6:1	AA-EQS Inland waters [19]		LOQ S/N = 6:1	AA-EQS Inland waters [19]
	ng/L	ng/L		ng/L	ng/L
1,3,5-Trichlorobenzene	7.6	400	Acenaphthylene	10.4	-
1,2,4-Trichlorobenzene	10.6	400	Acenaphthene	15.0	-
Naphthalene	38.0	2400	Pentachlorobenzene	7.4	7
Hexachlorobutadiene	15.2	100	Fluorene	11.4	-
1,2,3-Trichlorobenzene	8.0	400	Trifluralin	24.4	30

7.4.4 Calibration (with and without sediment)

Table 7.9: Equation of calibration (y = b • x + a) and the belonging correlation coefficient (r) for analyte (5 – 50 ng/L), sediment (250 mg - 1000 mg) and analyte and sediment (ca. 27.5 ng/L + 250 - 1000 mg sediment) spiked surface water samples

	Linearity Analytes			Linearity Sediment (PAH-Loamy Clay)			Linearity Analytes and sediment		
	a	b	r	a	b	r	a	b	r
1,3,5-Trichlorobenzene	2406.3	770.1	0.9942		n.d.			c.a.c.	
1,2,4-Trichlorobenzene	392.2	1127.5	0.9991		n.d.			c.a.c.	
Naphthalene	116293.2	4326.0	0.9826	266715.4	1495.8	0.9873	66739.0	3888.1	0.9974
Hexachlorobutadiene	-40.2	513.7	0.9971		n.d.			c.a.c.	
1,2,3-Trichlorobenzene	-47.2	1297.4	0.9958		n.d.			c.a.c.	
Acenaphthylene	-2145.4	4297.6	0.9963	-9621.5	132.8	0.9905	52653.2	2392.6	0.9957
Acenaphthene	6152.1	3217.1	0.9962	3234.7	22.4	0.9976	68996.8	788.7	0.9977
Pentachlorobenzene	-1246.8	1491.2	0.9929		n.d.			c.a.c.	
Fluorene	1543.6	3568.4	0.9952	9671.7	76.1	0.9973	83975.6	197.4	0.9963
Trifluralin	-398.2	403.1	0.9908		n.d.			c.a.c.	
alpha-HCH	164.2	298.9	0.9970	257.1	15.5	0.9915	-4837.0	384.3	0.9999
Hexachlorobenzene	817.5	690.4	0.9982	-622.1	42.0	0.9986	-17271.6	1165.2	0.9974
Simazine	81.4	51.4	0.9928		n.d.			c.a.c.	
Atrazine	-37.3	448.2	0.9969		n.d.			c.a.c.	
beta-HCH	-586.8	276.6	0.9643	36.0	7.4	0.9987	738.9	236.4	0.9199

Table 7.9: Equation of calibration (y = b • x + a) and the belonging correlation coefficient (r) for analyte (5 – 50 ng/L), sediment (250 mg - 1000 mg) and analyte and sediment (ca. 27.5 ng/L + 250 - 1000 mg sediment) spiked surface water samples (continued)

	Linearity Analytes			Linearity Sediment (PAH-Loamy Clay)			Linearity Analytes and sediment		
	a	b	r	a	b	r	a	b	r
gamma-HCH	205.6	228.6	0.9974	-341.6	3.5	0.9899	-5338.1	353.7	0.8998
Phenanthrene	5348.8	769.6	0.9949	-1670.4	609.9	0.9990	-43654.2	978.9	0.9994
Anthracene	6727.4	2995.9	0.9929	-2357.2	152.3	0.9711	-213116.0	10512.2	0.9974
delta-HCH	195.3	173.4	0.9917		n.d.			c.a.c.	
PCB 28	-7920.7	2000.0	0.9892	-639.3	87.3	0.9981	-5545.5	1760.5	0.9997
Alachlor	152.0	340.7	0.9919		n.d.			c.a.c.	
PCB 52	-4291.0	1481.1	0.9921	1737.5	97.0	0.9989	-6690.7	1452.5	0.9995
Chlorpyrifos-ethyl	431.7	200.8	0.9910		n.d.			c.a.c.	
Aldrin	91.6	189.2	0.9953	-32.4	4.1	0.9997	-3548.2	305.3	0.9528
Isodrin	-187.0	277.9	0.9726		n.d.			c.a.c.	
Chlorfenvinphos	657.6	189.7	0.9886		n.d.			c.a.c.	
Fluoranthene	9353.6	5626.9	0.9917	-42496.6	3155.0	0.9968	-159911.5	6037.3	0.9994
PCB 101	-2399.9	1394.8	0.9869	1020.3	66.1	0.9997	1528.9	1331.9	0.9960
Pyrene	13915.8	5452.1	0.9945	15466.5	575.5	0.9904	32380.3	2288.4	0.9980
alpha-Endosulfan	-334.3	88.8	0.9772	1292.3	6.8	0.9858	727.5	32.7	0.9060

Table 7.9**:** Equation of calibration (y = b • x + a) and the belonging correlation coefficient (r) for analyte (5 – 50 ng/L), sediment (250 mg - 1000 mg) and analyte and sediment (ca. 27.5 ng/L + 250 - 1000 mg sediment) spiked surface water samples (continued)

	Linearity Analytes			Linearity Sediment (PAH-Loamy Clay)			Linearity Analytes and sediment		
	a	b	r	a	b	r	a	b	r
p,p'-DDE	-119.4	568.9	0.9928	87.4	14.5	0.9982	-2989.0	706.8	0.9806
Dieldrin	-370.6	150.3	0.9849	240.7	3.7	0.9950	-1355.6	160.3	0.9931
Endrin	-301.3	150.8	0.9875		n.d.		1929.3	53.9	1.0000
beta-Endosulfan	123.1	86.1	0.9731		n.d.			c.a.c.	
BDE 28	-2532.7	576.4	0.9853		n.d.			c.a.c.	
p,p'-TDE	851.2	878.9	0.9972		n.d.			c.a.c.	
o,p'-DDT	958.0	613.0	0.9969	-34.8	33.8	0.9971	-10130.9	817.2	0.9833
PCB 153	116.3	1095.1	0.9874	1915.2	51.6	0.9980	3197.8	1162.6	0.9977
p,p'-DDT	857.7	538.7	0.9968	-280.5	7.0	0.9785	-12088.2	800.0	0.9824
PCB 138	691.0	1000.6	0.9933	833.3	78.1	0.9981	2138.4	1136.4	0.9996
Benz[a]anthracene	-380.5	3558.8	0.9955	5969.2	733.8	0.9937	16755.6	2452.0	0.9975
Chrysene	870.0	4910.8	0.9961	-19031.0	1823.8	0.9972	-51734.4	4681.0	0.9975
PCB 180	880.3	771.9	0.9927	829.2	56.2	0.9991	1985.2	956.3	1.0000
BDE 47	-1519.6	491.4	0.9895		n.d.			c.a.c.	
BDE 100	-124.2	31.9	0.9801		n.d.			c.a.c.	

Table 7.9: Equation of calibration (y = b • x + a) and the belonging correlation coefficient (r) for analyte (5 – 50 ng/L), sediment (250 mg - 1000 mg) and analyte and sediment (ca. 27.5 ng/L + 250 - 1000 mg sediment) spiked surface water samples (continued)

	Linearity Analytes			Linearity Sediment (PAH-Loamy Clay)			Linearity Analytes and sediment		
	a	b	r	a	b	r	a	b	r
Benzo[b]fluoranthene	2117.6	2923.4	0.9960	40990.3	687.0	0.9683	-21960.7	3599.1	0.9986
BDE 99	-147.6	26.4	0.9891		n.d.			c.a.c.	
Benzo[k]fluoranthene	13474.7	4131.6	0.9950	-79529.4	1583.3	0.9910	7841.7	3504.0	0.9998
Benzo[a]pyrene	-1055.3	2535.6	0.9913	1623.1	26.6	0.9924	36410.1	1016.7	0.9990
BDE 154	-199.7	48.0	0.9911		n.d.			c.a.c.	
BDE 153	-208.6	44.8	0.9920		n.d.			c.a.c.	
Indeno[1,2,3-c,d]pyrene	-630.5	1837.8	0.9964	-21073.2	538.0	0.9902	5191.3	2751.6	1.0000
Dibenzo[a,h]-anthracene	427.8	2287.0	0.9963	-100091.3	1194.8	0.9966	35379.8	3686.6	1.0000
Benzo[g,h,i]perylene	4806.8	2906.8	0.9989	-2355.4	295.6	0.9762	18791.7	2702.9	0.9976

n.d.: not detected, c.a.c.: constant analyte concentration

Figure 7.4: Water samples containing different amounts and kinds of certificated sediment; from left to right: 250 mg, 500 mg, 1000 mg PAH Loamy Clay 1 and 1000 mg EC 3 sediment in 1 L tap water

7.4.5 Comparison with alternative methods

Table 7.10: Recoveries of alternative sample preparation methods; extraction of 500 mg EC 3 sediment and/or 50 ng/L analytes

	SPE disk extraction	LLE (n-hexane)			Soxhlet extraction (acetone)	Certified reference value for EC 3 sediment
	Sediment	Analytes	Sediment	Analytes and sediment	Sediment	Weight per cent
	%	%	%	%	%	ng/g
1,3,5-Trichlorobenzene	27	73	15	37	27	114 ± 10
1,2,4-Trichlorobenzene	33	71	16	35	34	141 ± 14
Naphthalene	135	74	78	62	140	35 ± 20
Hexachlorobutadiene	36	69	16	64	36	61 ± 7
1,2,3-Trichlorobenzene	28	74	18	63	33	9 ± 1
Acenaphthylene	81	74	49	62	144	25 ± 8
Acenaphthene	86	76	41	64	50	22 ± 9
Pentachlorobenzene	59	77	35	54	51	65 ± 8
Fluorene	51	80	21	57	26	42 ± 21
Trifluralin	n.d.	79	n.d.	77	n.d.	n.d.
alpha-HCH	n.d.	82	n.d.	77	n.d.	n.d.
Hexachlorobenzene	78	80	40	46	54	279 ± 33
Simazine	n.d.	n.d.	n.d.	6	n.d.	n.d.
Atrazine	n.d.	2	n.d.	2	n.d.	n.d.
beta-HCH	n.d.	62	n.d.	63	n.d.	n.d.
gamma-HCH	n.d.	79	n.d.	77	n.d.	n.d.
Phenanthrene	85	86	38	48	55	293 ± 33
Anthracene	83	86	30	168	95	59 ± 11
delta-HCH	n.d.	134	n.d.	119	n.d.	n.d.
PCB 28	57	86	30	66	97	18.6 ± 8.6
Alachlor	n.d.	65	n.d.	59	n.d.	n.d.
PCB 52	83	87	44	61	84	35.6 ± 12.9
Chlorpyrifos-ethyl	n.d.	98	n.d.	97	n.d.	n.d.
Aldrin	n.d.	80	n.d.	61	n.d.	n.d.
Isodrin	n.d.	86	n.d.	68	n.d.	n.d.
Chlorfenvinphos	n.d.	82	n.d.	81	n.d.	n.d.
Fluoranthene	88	96	47	53	73	558 ± 46
PCB 101	101	91	31	51	57	38.3 ± 7.2

Table 7.10: Recoveries of alternative sample preparation methods; extraction of 500 mg EC 3 sediment and/or 50 ng/L analytes (continued)

	SPE disk extraction	LLE (n-hexane)			Soxhlet extraction (acetone)	Certified reference value for EC 3 sediment
	Sediment	Analytes	Sediment	Analytes and sediment	Sediment	Weight per cent
	%	%	%	%	%	ng/g
Pyrene	99	96	51	55	89	436 ± 47
alpha-Endosulfan	n.d.	99	n.d.	87	n.d.	n.d.
p,p'-DDE	n.d.	92	n.d.	70	n.d.	n.d.
Dieldrin	n.d.	87	n.d.	86	n.d.	n.d.
Endrin	n.d.	93	n.d.	97	n.d.	n.d.
beta-Endosulfan	n.d.	94	n.d.	85	n.d.	n.d.
p,p'-TDE	n.d.	95	n.d.	90	n.d.	n.d.
o,p'-DDT	n.d.	96	n.d.	64	n.d.	n.d.
PCB 153	90	94	22	45	74	24.2 ± 4.1
p,p'-DDT	n.d.	98	n.d.	60	n.d.	n.d.
PCB 138	106	93	25	45	91	25.2 ± 6.3
Benz[a]anthracene	116	101	35	42	122	312± 28
Chrysene	72	91	28	31	81	458 ± 59[(a)]
PCB 180	88	115	18	40	91	15.4 ± 6.6
Benzo[b]fluoranthene	88	108	26	27	184	505 ± 88
Benzo[k]fluoranthene	124	97	40	37	131	271 ± 104
Benzo[a]pyrene	130	96	37	34	214	386 ± 50
Indeno[1,2,3-c,d]pyrene	118	88	32	34	188	359 ± 36
Dibenzo[a,h]anthracene	88	90	18	23	83	109 ± 17
Benzo[g,h,i]perylene	133	92	30	28	171	348 ± 70

(a) Reference value of the sum of Chrysene and Triphenylene, n.d.: not detected

7.4.6 References

[1] Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council (2008).

7.5 Determination of organic priority pollutants in the low ng/L-range in water by solid phase extraction disk combined with large volume injection/gas chromatography-mass spectrometry

7.5.1 Solutions

Table 7.11: Preparation of mixed solution by diluting diluted standard solutions in acetone

Name	Solution	Volume	Flask size	Substance	Final concentration
		mL	mL		µg/L
Mix solution, 500 µg/L	PAH - mix, 10 mg/L	0.050	1	Acenaphthene	500.0
				Acenaphthylene	500.0
				Anthracene	500.0
				Benzo[a]anthracene	500.0
				Benzo[a]pyrene	500.0
				Benzo[b]fluoranthene	500.0
				Benzo[g,h,i]perylene	500.0
				Benzo[k]fluoranthene	500.0
				Chrysene	500.0
				Dibenzo[a,h]anthracene	500.0
				Fluoranthene	500.0
				Fluorene	500.0
				Indeno[1,2,3-c,d]pyrene	500.0
				Naphthalene	500.0
				Phenanthrene	500.0
				Pyrene	500.0
	PSM - mix, 10 mg/L	0.050		Alachlor	500.0
				Aldrin	502.5
				Atrazine	490.0
				Chlorfenvinphos	550.0
				Chlorpyrifos-ethyl	495.0
				p,p'-DDE	490.0
				p,p'-TDE	532.5
				p,p'-DDT	490.0
				o,p'-DDT	510.0
				Dieldrin	487.5
				alpha-Endosulfan	510.0
				beta-Endosulfan	570.0
				Endrin	520.0
				Hexachlorobenzene	515.0
				Hexachlorobutadiene	545.0
				alpha-HCH	485.0
				beta-HCH	482.5
				gamma-HCH	545.0
				delta-HCH	520.0

Table 7.11: Preparation of mixed solution by diluting diluted standard solutions in acetone (continued)

Name	Solution	Volume	Flask size	Substance	Final concentration
		mL	mL		µg/L
Mix solution, 500 µg/L (continued)				Isodrin	495.0
				Pentachlorobenzene	492.5
				Simazine	510.0
				1,2,3-Trichlorobenzene	500.0
				1,2,4-Trichlorobenzene	550.0
				1,3,5-Trichlorobenzene	475.0
				Trifluralin	495.0
	PCB mix, 10 mg/L	0.050		PCB 28	500.0
				PCB 52	500.0
				PCB 101	500.0
				PCB 138	500.0
				PCB 153	500.0
				PCB 180	500.0
	BDE - mix, 1 mg/L	0.500		BDE 28	500.0
				BDE 47	500.0
				BDE 99	500.0
				BDE 100	500.0
				BDE 153	500.0
				BDE 154	500.0
Mix solution, 50 µg/L	PAH - mix, 1 mg/L	0.1	2	Acenaphthene	50.0
				Acenaphthylene	50.0
				Anthracene	50.0
				Benzo[a]anthracene	50.0
				Benzo[a]pyrene	50.0
				Benzo[b]fluoranthene	50.0
				Benzo[g,h,i]perylene	50.0
				Benzo[k]fluoranthene	50.0
				Chrysene	50.0
				Dibenzo[a,h]anthracene	50.0
				Fluoranthene	50.0
				Fluorene	50.0
				Indeno[1,2,3-c,d]pyrene	50.0
				Naphthalene	50.0
				Phenanthrene	50.0
				Pyrene	50.0

Table 7.11: Preparation of mixed solution by diluting diluted standard solutions in acetone (continued)

Name	Solution	Volume	Flask size	Substance	Final concentration
		mL	mL		µg/L
Mix solution, 50 µg/L (continued)	PSM - mix, 1 mg/L	0.100		Alachlor	50.0
				Aldrin	50.3
				Atrazine	49.0
				Chlorfenvinphos	55.0
				Chlorpyrifos-ethyl	49.5
				p,p'-DDE	49.0
				p,p'-TDE	53.3
				p,p'-DDT	49.0
				o,p'-DDT	51.0
				Dieldrin	48.8
				alpha-Endosulfan	51.0
				beta-Endosulfan	57.0
				Endrin	52.0
				Hexachlorobenzene	51.5
				Hexachlorobutadiene	54.5
				alpha-HCH	48.5
				beta-HCH	48.3
				gamma-HCH	54.5
				delta-HCH	52.0
				Isodrin	49.5
				Pentachlorobenzene	49.3
				Simazine	51.0
				1,2,3-Trichlorobenzene	50.0
				1,2,4-Trichlorobenzene	55.0
				1,3,5-Trichlorobenzene	47.5
				Trifluralin	49.5
	PCB mix, 1 mg/L	0.100		PCB 28	50.0
				PCB 52	50.0
				PCB 101	50.0
				PCB 138	50.0
				PCB 153	50.0
				PCB 180	50.0

Table 7.11: Preparation of mixed solution by diluting diluted standard solutions in acetone (continued)

Name	Solution	Volume	Flask size	Substance	Final concentration
		mL	mL		µg/L
Mix solution, 50 µg/L (continued)	BDE - mix, 1 mg/L	0.100		BDE 28	50.0
				BDE 47	50.0
				BDE 99	50.0
				BDE 100	50.0
				BDE 153	50.0
				BDE 154	50.0

Table 7.12: Preparation of the volumetric standard (VS); solvent: acetone, flask size: 10 mL; spike volume: 100 µL, final eluate volume: 1.5 mL

Name	Solution	Volume	Substance	Final concentration	Concentration sample
		mL		mg/L	µg/L
Volumetric standard (VS), 250 µg/L	Volumetric standard (VS), 10 mg/L	0.250	Fluoranthene-D_{10}	0.263	17.5
			PCB 208	0.250	16.6

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike I	Mix solution, 50 µg/L	0.025	Acenaphthene	1.25	0.25
			Acenaphthylene	1.25	0.25
			Anthracene	1.25	0.25
			Benzo[a]anthracene	1.25	0.25
			Benzo[a]pyrene	1.25	0.25
			Benzo[b]fluoranthene	1.25	0.25
			Benzo[g,h,i]perylene	1.25	0.25
			Benzo[k]fluoranthene	1.25	0.25
			Chrysene	1.25	0.25
			Dibenzo[a,h]anthracene	1.25	0.25
			Fluoranthene	1.25	0.25
			Fluorene	1.25	0.25
			Indeno[1,2,3-c,d]pyrene	1.25	0.25
			Naphthalene	1.25	0.25
			Phenanthrene	1.25	0.25
			Pyrene	1.25	0.25
			Alachlor	1.25	0.25
			Aldrin	1.26	0.25
			Atrazine	1.23	0.25
			Chlorfenvinphos	1.38	0.26
			Chlorpyrifos-ethyl	1.24	0.25
			p,p'-DDE	1.22	0.25
			p,p'-TDE	1.33	0.27
			p,p'-DDT	1.22	0.25
			o,p'-DDT	1.28	0.26
			Dieldrin	1.22	0.24
			alpha-Endosulfan	1.28	0.26
			beta-Endosulfan	1.43	0.29
			Endrin	1.30	0.26
			Hexachlorobenzene	1.29	0.26
			Hexachlorobutadiene	1.36	0.27
			alpha-HCH	1.21	0.24
			beta-HCH	1.20	0.24
			gamma-HCH	1.36	0.27
			delta-HCH	1.30	0.26

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike I (continued)			Isodrin	1.24	0.25
			Pentachlorobenzene	1.23	0.25
			Simazine	1.28	0.26
			1,2,3-Trichlorobenzene	1.25	0.25
			1,2,4-Trichlorobenzene	1.38	0.28
			1,3,5-Trichlorobenzene	1.19	0.24
			Trifluralin	1.24	0.25
			PCB 28	1.25	0.25
			PCB 52	1.25	0.25
			PCB 101	1.25	0.25
			PCB 138	1.25	0.25
			PCB 153	1.25	0.25
			PCB 180	1.25	0.25
			BDE 28	1.25	0.25
			BDE 47	1.25	0.25
			BDE 99	1.25	0.25
			BDE 100	1.25	0.25
			BDE 153	1.25	0.25
			BDE 154	1.25	0.25

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike II	Mix solution, 50 µg/L	0.060	Acenaphthene	3.00	0.60
			Acenaphthylene	3.00	0.60
			Anthracene	3.00	0.60
			Benzo[a]anthracene	3.00	0.60
			Benzo[a]pyrene	3.00	0.60
			Benzo[b]fluoranthene	3.00	0.60
			Benzo[g,h,i]perylene	3.00	0.60
			Benzo[k]fluoranthene	3.00	0.60
			Chrysene	3.00	0.60
			Dibenzo[a,h]anthracene	3.00	0.60
			Fluoranthene	3.00	0.60
			Fluorene	3.00	0.60
			Indeno[1,2,3-c,d]pyrene	3.00	0.60
			Naphthalene	3.00	0.60
			Phenanthrene	3.00	0.60
			Pyrene	3.00	0.60
			Alachlor	3.00	0.60
			Aldrin	3.02	0.60
			Atrazine	2.94	0.59
			Chlorfenvinphos	3.30	0.66
			Chlorpyrifos-ethyl	2.97	0.59
			p,p'-DDE	2.94	0.59
			p,p'-TDE	3.20	0.64
			p,p'-DDT	2.94	0.59
			o,p'-DDT	3.06	0.61
			Dieldrin	2.93	0.59
			alpha-Endosulfan	3.06	0.61
			beta-Endosulfan	3.42	0.68
			Endrin	3.12	0.62
			Hexachlorobenzene	3.09	0.62
			Hexachlorobutadiene	3.27	0.65
			alpha-HCH	2.91	0.58
			beta-HCH	2.90	0.58
			gamma-HCH	3.27	0.65
			delta-HCH	3.12	0.62

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike II (continued)			Isodrin	2.97	0.59
			Pentachlorobenzene	2.96	0.59
			Simazine	3.06	0.61
			1,2,3-Trichlorobenzene	3.00	0.60
			1,2,4-Trichlorobenzene	3.30	0.66
			1,3,5-Trichlorobenzene	2.85	0.57
			Trifluralin	2.97	0.59
			PCB 28	3.00	0.60
			PCB 52	3.00	0.60
			PCB 101	3.00	0.60
			PCB 138	3.00	0.60
			PCB 153	3.00	0.60
			PCB 180	3.00	0.60
			BDE 28	3.00	0.60
			BDE 47	3.00	0.60
			BDE 99	3.00	0.60
			BDE 100	3.00	0.60
			BDE 153	3.00	0.60
			BDE 154	3.00	0.60

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike III	Mix solution, 50 µg/L	0.100	Acenaphthene	5.00	1.00
			Acenaphthylene	5.00	1.00
			Anthracene	5.00	1.00
			Benzo[a]anthracene	5.00	1.00
			Benzo[a]pyrene	5.00	1.00
			Benzo[b]fluoranthene	5.00	1.00
			Benzo[g,h,i]perylene	5.00	1.00
			Benzo[k]fluoranthene	5.00	1.00
			Chrysene	5.00	1.00
			Dibenzo[a,h]anthracene	5.00	1.00
			Fluoranthene	5.00	1.00
			Fluorene	5.00	1.00
			Indeno[1,2,3-c,d]pyrene	5.00	1.00
			Naphthalene	5.00	1.00
			Phenanthrene	5.00	1.00
			Pyrene	5.00	1.00
			Alachlor	5.00	1.00
			Aldrin	5.03	1.01
			Atrazine	4.90	0.98
			Chlorfenvinphos	5.50	1.10
			Chlorpyrifos-ethyl	4.95	0.99
			p,p'-DDE	4.90	0.98
			p,p'-TDE	5.33	1.07
			p,p'-DDT	4.90	0.98
			o,p'-DDT	5.10	1.02
			Dieldrin	4.88	0.975
			alpha-Endosulfan	5.10	1.02
			beta-Endosulfan	5.70	1.14
			Endrin	5.20	1.04
			Hexachlorobenzene	5.15	1.03
			Hexachlorobutadiene	5.45	1.09
			alpha-HCH	4.85	0.97
			beta-HCH	4.83	0.97
			gamma-HCH	5.45	1.09
			delta-HCH	5.20	1.04

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike III (continued)			Isodrin	4.95	0.99
			Pentachlorobenzene	4.93	0.99
			Simazine	5.10	1.02
			1,2,3-Trichlorobenzene	5.00	1.00
			1,2,4-Trichlorobenzene	5.50	1.10
			1,3,5-Trichlorobenzene	4.75	0.95
			Trifluralin	4.95	0.99
			PCB 28	5.00	1.00
			PCB 52	5.00	1.00
			PCB 101	5.00	1.00
			PCB 138	5.00	1.00
			PCB 153	5.00	1.00
			PCB 180	5.00	1.00
			BDE 28	5.00	1.00
			BDE 47	5.00	1.00
			BDE 99	5.00	1.00
			BDE 100	5.00	1.00
			BDE 153	5.00	1.00
			BDE 154	5.00	1.00

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike IV	Mix solution, 50 µg/L	0.130	Acenaphthene	6.50	1.30
			Acenaphthylene	6.50	1.30
			Anthracene	6.50	1.30
			Benzo[a]anthracene	6.50	1.30
			Benzo[a]pyrene	6.50	1.30
			Benzo[b]fluoranthene	6.50	1.30
			Benzo[g,h,i]perylene	6.50	1.30
			Benzo[k]fluoranthene	6.50	1.30
			Chrysene	6.50	1.30
			Dibenzo[a,h]anthracene	6.50	1.30
			Fluoranthene	6.50	1.30
			Fluorene	6.50	1.30
			Indeno[1,2,3-c,d]pyrene	6.50	1.30
			Naphthalene	6.50	1.30
			Phenanthrene	6.50	1.30
			Pyrene	6.50	1.30
			Alachlor	6.50	1.30
			Aldrin	6.53	1.31
			Atrazine	6.37	1.27
			Chlorfenvinphos	7.15	1.43
			Chlorpyrifos-ethyl	6.43	1.29
			p,p'-DDE	6.37	1.27
			p,p'-TDE	6.92	1.38
			p,p'-DDT	6.37	1.27
			o,p'-DDT	6.63	1.33
			Dieldrin	6.33	1.27
			alpha-Endosulfan	6.63	1.33
			beta-Endosulfan	7.41	1.48
			Endrin	6.76	1.35
			Hexachlorobenzene	6.70	1.34
			Hexachlorobutadiene	7.09	1.42
			alpha-HCH	6.31	1.26
			beta-HCH	6.27	1.25
			gamma-HCH	7.09	1.42
			delta-HCH	6.76	1.35

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike IV (continued)			Isodrin	6.44	1.29
			Pentachlorobenzene	6.40	1.28
			Simazine	6.63	1.33
			1,2,3-Trichlorobenzene	6.50	1.30
			1,2,4-Trichlorobenzene	7.15	1.43
			1,3,5-Trichlorobenzene	6.18	1.24
			Trifluralin	6.44	1.29
			PCB 28	6.50	1.30
			PCB 52	6.50	1.30
			PCB 101	6.50	1.30
			PCB 138	6.50	1.30
			PCB 153	6.50	1.30
			PCB 180	6.50	1.30
			BDE 28	6.50	1.30
			BDE 47	6.50	1.30
			BDE 99	6.50	1.30
			BDE 100	6.50	1.30
			BDE 153	6.50	1.30
			BDE 154	6.50	1.30

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike V	Mix solution, 50 µg/L	0.175	Acenaphthene	8.75	1.75
			Acenaphthylene	8.75	1.75
			Anthracene	8.75	1.75
			Benzo[a]anthracene	8.75	1.75
			Benzo[a]pyrene	8.75	1.75
			Benzo[b]fluoranthene	8.75	1.75
			Benzo[g,h,i]perylene	8.75	1.75
			Benzo[k]fluoranthene	8.75	1.75
			Chrysene	8.75	1.75
			Dibenzo[a,h]anthracene	8.75	1.75
			Fluoranthene	8.75	1.75
			Fluorene	8.75	1.75
			Indeno[1,2,3-c,d]pyrene	8.75	1.75
			Naphthalene	8.75	1.75
			Phenanthrene	8.75	1.75
			Pyrene	8.75	1.75
			Alachlor	8.75	1.75
			Aldrin	8.79	1.76
			Atrazine	8.58	1.72
			Chlorfenvinphos	9.63	1.93
			Chlorpyrifos-ethyl	8.66	1.73
			p,p'-DDE	8.58	1.72
			p,p'-TDE	9.32	1.86
			p,p'-DDT	8.58	1.72
			o,p'-DDT	8.93	1.79
			Dieldrin	8.53	1.71
			alpha-Endosulfan	8.93	1.79
			beta-Endosulfan	9.98	2.00
			Endrin	9.10	1.82
			Hexachlorobenzene	9.01	1.80
			Hexachlorobutadiene	9.54	1.91
			alpha-HCH	8.49	1.70
			beta-HCH	8.44	1.69
			gamma-HCH	9.54	1.91
			delta-HCH	9.01	1.82

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike V (continued)			Isodrin	8.66	1.73
			Pentachlorobenzene	8.62	1.72
			Simazine	8.93	1.79
			1,2,3-Trichlorobenzene	8.75	1.75
			1,2,4-Trichlorobenzene	9.63	1.93
			1,3,5-Trichlorobenzene	8.32	1.66
			Trifluralin	8.66	1.73
			PCB 28	8.75	1.75
			PCB 52	8.75	1.75
			PCB 101	8.75	1.75
			PCB 138	8.75	1.75
			PCB 153	8.75	1.75
			PCB 180	8.75	1.75
			BDE 28	8.75	1.75
			BDE 47	8.75	1.75
			BDE 99	8.75	1.75
			BDE 100	8.75	1.75
			BDE 153	8.75	1.75
			BDE 154	8.75	1.75

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike VI	Mix solution, 50 µg/L	0.210	Acenaphthene	10.50	2.10
			Acenaphthylene	10.50	2.10
			Anthracene	10.50	2.10
			Benzo[a]anthracene	10.50	2.10
			Benzo[a]pyrene	10.50	2.10
			Benzo[b]fluoranthene	10.50	2.10
			Benzo[g,h,i]perylene	10.50	2.10
			Benzo[k]fluoranthene	10.50	2.10
			Chrysene	10.50	2.10
			Dibenzo[a,h]anthracene	10.50	2.10
			Fluoranthene	10.50	2.10
			Fluorene	10.50	2.10
			Indeno[1,2,3-c,d]pyrene	10.50	2.10
			Naphthalene	10.50	2.10
			Phenanthrene	10.50	2.10
			Pyrene	10.50	2.10
			Alachlor	10.50	2.10
			Aldrin	10.55	2.11
			Atrazine	10.29	2.06
			Chlorfenvinphos	11.55	2.31
			Chlorpyrifos-ethyl	10.40	2.08
			p,p'-DDE	10.29	2.06
			p,p'-TDE	11.18	2.24
			p,p'-DDT	10.29	2.06
			o,p'-DDT	10.71	2.14
			Dieldrin	10.24	2.05
			alpha-Endosulfan	10.71	2.14
			beta-Endosulfan	11.97	2.39
			Endrin	10.92	2.18
			Hexachlorobenzene	10.82	2.16
			Hexachlorobutadiene	11.45	2.29
			alpha-HCH	10.19	2.04
			beta-HCH	10.13	2.03
			gamma-HCH	11.45	2.29
			delta-HCH	10.92	2.18

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike VI (continued)			Isodrin	10.40	2.08
			Pentachlorobenzene	10.34	2.07
			Simazine	10.71	2.14
			1,2,3-Trichlorobenzene	10.50	2.10
			1,2,4-Trichlorobenzene	11.55	2.31
			1,3,5-Trichlorobenzene	9.98	2.00
			Trifluralin	10.40	2.08
			PCB 28	10.50	2.10
			PCB 52	10.50	2.10
			PCB 101	10.50	2.10
			PCB 138	10.50	2.10
			PCB 153	10.50	2.10
			PCB 180	10.50	2.10
			BDE 28	10.50	2.10
			BDE 47	10.50	2.10
			BDE 99	10.50	2.10
			BDE 100	10.50	2.10
			BDE 153	10.50	2.10
			BDE 154	10.50	2.10

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike VII*	Mix solution, 500 µg/L	0.125	Acenaphthene	12.50	2.50
			Acenaphthylene	12.50	2.50
			Anthracene	12.50	2.50
			Benzo[a]anthracene	12.50	2.50
			Benzo[a]pyrene	12.50	2.50
			Benzo[b]fluoranthene	12.50	2.50
			Benzo[g,h,i]perylene	12.50	2.50
			Benzo[k]fluoranthene	12.50	2.50
			Chrysene	12.50	2.50
			Dibenzo[a,h]anthracene	12.50	2.50
			Fluoranthene	12.50	2.50
			Fluorene	12.50	2.50
			Indeno[1,2,3-c,d]pyrene	12.50	2.50
			Naphthalene	12.50	2.50
			Phenanthrene	12.50	2.50
			Pyrene	12.50	2.50
			Alachlor	12.50	2.50
			Aldrin	12.56	2.51
			Atrazine	12.25	2.45
			Chlorfenvinphos	13.75	2.75
			Chlorpyrifos-ethyl	12.38	2.48
			p,p'-DDE	12.25	2.45
			p,p'-TDE	13.31	2.66
			p,p'-DDT	12.25	2.45
			o,p'-DDT	12.75	2.55
			Dieldrin	12.19	2.44
			alpha-Endosulfan	12.75	2.55
			beta-Endosulfan	14.25	2.85
			Endrin	13.00	2.60
			Hexachlorobenzene	12.88	2.58
			Hexachlorobutadiene	13.63	2.73
			alpha-HCH	12.12	2.43
			beta-HCH	12.06	2.41
			gamma-HCH	13.63	2.73
			delta-HCH	13.00	2.60

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike VII* (continued)			Isodrin	12.38	2.48
			Pentachlorobenzene	12.31	2.46
			Simazine	12.75	2.55
			1,2,3-Trichlorobenzene	12.50	2.50
			1,2,4-Trichlorobenzene	13.75	2.75
			1,3,5-Trichlorobenzene	11.88	2.38
			Trifluralin	12.38	2.48
			PCB 28	12.50	2.50
			PCB 52	12.50	2.50
			PCB 101	12.50	2.50
			PCB 138	12.50	2.50
			PCB 153	12.50	2.50
			PCB 180	12.50	2.50
			BDE 28	12.50	2.50
			BDE 47	12.50	2.50
			BDE 99	12.50	2.50
			BDE 100	12.50	2.50
			BDE 153	12.50	2.50
			BDE 154	12.50	2.50

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike VIII	Mix solution, 500 µg/L	0.060	Acenaphthene	30.0	6.0
			Acenaphthylene	30.0	6.0
			Anthracene	30.0	6.0
			Benzo[a]anthracene	30.0	6.0
			Benzo[a]pyrene	30.0	6.0
			Benzo[b]fluoranthene	30.0	6.0
			Benzo[g,h,i]perylene	30.0	6.0
			Benzo[k]fluoranthene	30.0	6.0
			Chrysene	30.0	6.0
			Dibenzo[a,h]anthracene	30.0	6.0
			Fluoranthene	30.0	6.0
			Fluorene	30.0	6.0
			Indeno[1,2,3-c,d]pyrene	30.0	6.0
			Naphthalene	30.0	6.0
			Phenanthrene	30.0	6.0
			Pyrene	30.0	6.0
			Alachlor	30.0	6.0
			Aldrin	30.2	6.0
			Atrazine	29.4	5.9
			Chlorfenvinphos	33.0	6.6
			Chlorpyrifos-ethyl	29.7	5.9
			p,p'-DDE	29.4	5.9
			p,p'-TDE	32.0	6.4
			p,p'-DDT	29.4	5.9
			o,p'-DDT	30.1	6.1
			Dieldrin	29.3	5.9
			alpha-Endosulfan	30.6	6.1
			beta-Endosulfan	34.2	6.8
			Endrin	31.2	6.2
			Hexachlorobenzene	30.9	6.2
			Hexachlorobutadiene	32.7	6.5
			alpha-HCH	29.1	5.8
			beta-HCH	29.0	5.8
			gamma-HCH	32.7	6.5
			delta-HCH	31.2	6.2

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike VIII (continued)			Isodrin	29.7	5.9
			Pentachlorobenzene	29.6	5.9
			Simazine	30.6	6.1
			1,2,3-Trichlorobenzene	30.0	6.0
			1,2,4-Trichlorobenzene	33.0	6.6
			1,3,5-Trichlorobenzene	28.5	5.7
			Trifluralin	29.7	5.94
			PCB 28	30.0	6.0
			PCB 52	30.0	6.0
			PCB 101	30.0	6.0
			PCB 138	30.0	6.0
			PCB 153	30.0	6.0
			PCB 180	30.0	6.0
			BDE 28	30.0	6.0
			BDE 47	30.0	6.0
			BDE 99	30.0	6.0
			BDE 100	30.0	6.0
			BDE 153	30.0	6.0
			BDE 154	30.0	6.0

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike IX	Mix solution, 500 µg/L	0.100	Acenaphthene	50.0	10.0
			Acenaphthylene	50.0	10.0
			Anthracene	50.0	10.0
			Benzo[a]anthracene	50.0	10.0
			Benzo[a]pyrene	50.0	10.0
			Benzo[b]fluoranthene	50.0	10.0
			Benzo[g,h,i]perylene	50.0	10.0
			Benzo[k]fluoranthene	50.0	10.0
			Chrysene	50.0	10.0
			Dibenzo[a,h]anthracene	50.0	10.0
			Fluoranthene	50.0	10.0
			Fluorene	50.0	10.0
			Indeno[1,2,3-c,d]pyrene	50.0	10.0
			Naphthalene	50.0	10.0
			Phenanthrene	50.0	10.0
			Pyrene	50.0	10.0
			Alachlor	50.0	10.0
			Aldrin	50.3	10.1
			Atrazine	49.0	9.8
			Chlorfenvinphos	55.0	11.0
			Chlorpyrifos-ethyl	49.5	9.9
			p,p'-DDE	49.0	9.8
			p,p'-TDE	53.3	10.7
			p,p'-DDT	49.0	9.8
			o,p'-DDT	51.0	10.2
			Dieldrin	48.8	9.8
			alpha-Endosulfan	51.0	10.2
			beta-Endosulfan	57.0	11.4
			Endrin	52.0	10.4
			Hexachlorobenzene	51.5	10.3
			Hexachlorobutadiene	54.5	10.9
			alpha-HCH	48.5	9.7
			beta-HCH	48.3	9.7
			gamma-HCH	54.5	10.9
			delta-HCH	52.0	10.4

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike IX (continued)			Isodrin	49.5	9.9
			Pentachlorobenzene	49.3	9.9
			Simazine	51.0	10.2
			1,2,3-Trichlorobenzene	50.0	10.0
			1,2,4-Trichlorobenzene	55.0	11.0
			1,3,5-Trichlorobenzene	47.5	9.5
			Trifluralin	49.5	9.9
			PCB 28	50.0	10.0
			PCB 52	50.0	10.0
			PCB 101	50.0	10.0
			PCB 138	50.0	10.0
			PCB 153	50.0	10.0
			PCB 180	50.0	10.0
			BDE 28	50.0	10.0
			BDE 47	50.0	10.0
			BDE 99	50.0	10.0
			BDE 100	50.0	10.0
			BDE 153	50.0	10.0
			BDE 154	50.0	10.0

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike X	Mix solution, 500 µg/L	0.130	Acenaphthene	65.0	13.0
			Acenaphthylene	65.0	13.0
			Anthracene	65.0	13.0
			Benzo[a]anthracene	65.0	13.0
			Benzo[a]pyrene	65.0	13.0
			Benzo[b]fluoranthene	65.0	13.0
			Benzo[g,h,i]perylene	65.0	13.0
			Benzo[k]fluoranthene	65.0	13.0
			Chrysene	65.0	13.0
			Dibenzo[a,h]anthracene	65.0	13.0
			Fluoranthene	65.0	13.0
			Fluorene	65.0	13.0
			Indeno[1,2,3-c,d]pyrene	65.0	13.0
			Naphthalene	65.0	13.0
			Phenanthrene	65.0	13.0
			Pyrene	65.0	13.0
			Alachlor	65.0	13.0
			Aldrin	65.3	13.1
			Atrazine	63.7	12.7
			Chlorfenvinphos	71.5	14.3
			Chlorpyrifos-ethyl	64.4	12.9
			p,p'-DDE	63.7	12.7
			p,p'-TDE	69.2	13.8
			p,p'-DDT	63.7	12.7
			o,p'-DDT	66.3	13.3
			Dieldrin	63.4	12.7
			alpha-Endosulfan	66.3	13.3
			beta-Endosulfan	74.1	14.8
			Endrin	67.6	13.5
			Hexachlorobenzene	67.0	13.4
			Hexachlorobutadiene	70.9	14.2
			alpha-HCH	63.1	12.6
			beta-HCH	62.7	12.5
			gamma-HCH	70.9	14.2
			delta-HCH	67.6	13.5

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike X (continued)			Isodrin	64.4	12.9
			Pentachlorobenzene	64.0	12.8
			Simazine	66.3	13.3
			1,2,3-Trichlorobenzene	65.0	13.0
			1,2,4-Trichlorobenzene	71.5	14.3
			1,3,5-Trichlorobenzene	61.8	12.4
			Trifluralin	64.4	12.9
			PCB 28	65.0	13.0
			PCB 52	65.0	13.0
			PCB 101	65.0	13.0
			PCB 138	65.0	13.0
			PCB 153	65.0	13.0
			PCB 180	65.0	13.0
			BDE 28	65.0	13.0
			BDE 47	65.0	13.0
			BDE 99	65.0	13.0
			BDE 100	65.0	13.0
			BDE 153	65.0	13.0
			BDE 154	65.0	13.0

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike XI	Mix solution, 500 µg/L	0.175	Acenaphthene	87.5	17.5
			Acenaphthylene	87.5	17.5
			Anthracene	87.5	17.5
			Benzo[a]anthracene	87.5	17.5
			Benzo[a]pyrene	87.5	17.5
			Benzo[b]fluoranthene	87.5	17.5
			Benzo[g,h,i]perylene	87.5	17.5
			Benzo[k]fluoranthene	87.5	17.5
			Chrysene	87.5	17.5
			Dibenzo[a,h]anthracene	87.5	17.5
			Fluoranthene	87.5	17.5
			Fluorene	87.5	17.5
			Indeno[1,2,3-c,d]pyrene	87.5	17.5
			Naphthalene	87.5	17.5
			Phenanthrene	87.5	17.5
			Pyrene	87.5	17.5
			Alachlor	87.5	17.5
			Aldrin	87.9	17.6
			Atrazine	85.8	17.2
			Chlorfenvinphos	96.3	19.3
			Chlorpyrifos-ethyl	86.6	17.3
			p,p'-DDE	85.8	17.2
			p,p'-TDE	93.2	18.6
			p,p'-DDT	85.8	17.2
			o,p'-DDT	89.3	17.9
			Dieldrin	85.3	17.1
			alpha-Endosulfan	89.3	17.9
			beta-Endosulfan	99.8	20.0
			Endrin	91.0	18.2
			Hexachlorobenzene	90.1	18.0
			Hexachlorobutadiene	95.4	19.1
			alpha-HCH	84.9	17.0
			beta-HCH	84.4	16.9
			gamma-HCH	95.4	19.1
			delta-HCH	91.0	18.2

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike XI (continued)			Isodrin	86.6	17.3
			Pentachlorobenzene	86.2	17.2
			Simazine	89.3	17.9
			1,2,3-Trichlorobenzene	87.5	17.5
			1,2,4-Trichlorobenzene	96.3	19.3
			1,3,5-Trichlorobenzene	83.1	16.6
			Trifluralin	86.6	17.3
			PCB 28	87.5	17.5
			PCB 52	87.5	17.5
			PCB 101	87.5	17.5
			PCB 138	87.5	17.5
			PCB 153	87.5	17.5
			PCB 180	87.5	17.5
			BDE 28	87.5	17.5
			BDE 47	87.5	17.5
			BDE 99	87.5	17.5
			BDE 100	87.5	17.5
			BDE 153	87.5	17.5
			BDE 154	87.5	17.5

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike XII	Mix solution, 500 µg/L	0.210	Acenaphthene	105.0	21.0
			Acenaphthylene	105.0	21.0
			Anthracene	105.0	21.0
			Benzo[a]anthracene	105.0	21.0
			Benzo[a]pyrene	105.0	21.0
			Benzo[b]fluoranthene	105.0	21.0
			Benzo[g,h,i]perylene	105.0	21.0
			Benzo[k]fluoranthene	105.0	21.0
			Chrysene	105.0	21.0
			Dibenzo[a,h]anthracene	105.0	21.0
			Fluoranthene	105.0	21.0
			Fluorene	105.0	21.0
			Indeno[1,2,3-c,d]pyrene	105.0	21.0
			Naphthalene	105.0	21.0
			Phenanthrene	105.0	21.0
			Pyrene	105.0	21.0
			Alachlor	105.0	21.0
			Aldrin	105.5	21.1
			Atrazine	102.9	20.6
			Chlorfenvinphos	115.5	23.1
			Chlorpyrifos-ethyl	104.0	20.8
			p,p'-DDE	102.9	20.6
			p,p'-TDE	111.8	22.4
			p,p'-DDT	102.9	20.6
			o,p'-DDT	107.1	21.4
			Dieldrin	102.4	20.5
			alpha-Endosulfan	107.1	21.4
			beta-Endosulfan	119.7	23.9
			Endrin	109.2	21.8
			Hexachlorobenzene	108.2	21.6
			Hexachlorobutadiene	114.4	22.9
			alpha-HCH	101.9	20.4
			beta-HCH	101.3	20.3
			gamma-HCH	114.5	22.9
			delta-HCH	109.2	21.8

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike XII (continued)			Isodrin	104.0	20.8
			Pentachlorobenzene	103.4	20.7
			Simazine	107.1	21.4
			1,2,3-Trichlorobenzene	105.0	21.0
			1,2,4-Trichlorobenzene	115.5	23.1
			1,3,5-Trichlorobenzene	99.8	20.0
			Trifluralin	104.0	20.8
			PCB 28	105.0	21.0
			PCB 52	105.0	21.0
			PCB 101	105.0	21.0
			PCB 138	105.0	21.0
			PCB 153	105.0	21.0
			PCB 180	105.0	21.0
			BDE 28	105.0	21.0
			BDE 47	105.0	21.0
			BDE 99	105.0	21.0
			BDE 100	105.0	21.0
			BDE 153	105.0	21.0
			BDE 154	105.0	21.0

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike XIII	PAH - mix, 1 mg/L	0.125	Acenaphthene	125.0	25.0
			Acenaphthylene	125.0	25.0
			Anthracene	125.0	25.0
			Benzo[a]anthracene	125.0	25.0
			Benzo[a]pyrene	125.0	25.0
			Benzo[b]fluoranthene	125.0	25.0
			Benzo[g,h,i]perylene	125.0	25.0
			Benzo[k]fluoranthene	125.0	25.0
			Chrysene	125.0	25.0
			Dibenzo[a,h]anthracene	125.0	25.0
			Fluoranthene	125.0	25.0
			Fluorene	125.0	25.0
			Indeno[1,2,3-c,d]pyrene	125.0	25.0
			Naphthalene	125.0	25.0
			Phenanthrene	125.0	25.0
			Pyrene	125.0	25.0
	PSM - mix, 1 mg/L	0.125	Alachlor	125.0	25.0
			Aldrin	125.6	25.1
			Atrazine	122.5	24.5
			Chlorfenvinphos	137.5	27.5
			Chlorpyrifos-ethyl	123.8	24.8
			p,p'-DDE	122.5	24.5
			p,p'-TDE	133.1	26.6
			p,p'-DDT	122.5	24.5
			o,p'-DDT	127.5	25.5
			Dieldrin	121.9	24.4
			alpha-Endosulfan	127.5	25.5
			beta-Endosulfan	142.5	28.5
			Endrin	130.0	26.0
			Hexachlorobenzene	128.8	25.8
			Hexachlorobutadiene	136.3	27.3
			alpha-HCH	121.3	24.3
			beta-HCH	120.6	24.1
			gamma-HCH	136.3	27.3
			delta-HCH	130.0	26.0

Table 7.13: Preparation of the used spike solutions for the method calibration in a range of 0.25 to 25 ng/L in sample; solvent: acetone, flask size: 1 mL (*5 mL); spike volume: 200 µL, sample volume: 1000 mL (continued)

Name	Solution	Volume mL	Substance	Final concentration µg/L	Concentration sample ng/L
Spike XIII (continued)			Isodrin	123.8	24.8
			Pentachlorobenzene	123.1	24.6
			Simazine	127.5	25.5
			1,2,3-Trichlorobenzene	125.0	25.0
			1,2,4-Trichlorobenzene	137.5	27.5
			1,3,5-Trichlorobenzene	118.8	23.8
			Trifluralin	123.8	24.8
	PCB - mix, 1 mg/L	0.125	PCB 28	125.0	25.0
			PCB 52	125.0	25.0
			PCB 101	125.0	25.0
			PCB 138	125.0	25.0
			PCB 153	125.0	25.0
			PCB 180	125.0	25.0
	BDE - mix, 1 mg/L	0.125	BDE 28	125.0	25.0
			BDE 47	125.0	25.0
			BDE 99	125.0	25.0
			BDE 100	125.0	25.0
			BDE 153	125.0	25.0
			BDE 154	125.0	25.0

7.5.2 LVI-GC/MS optimisation

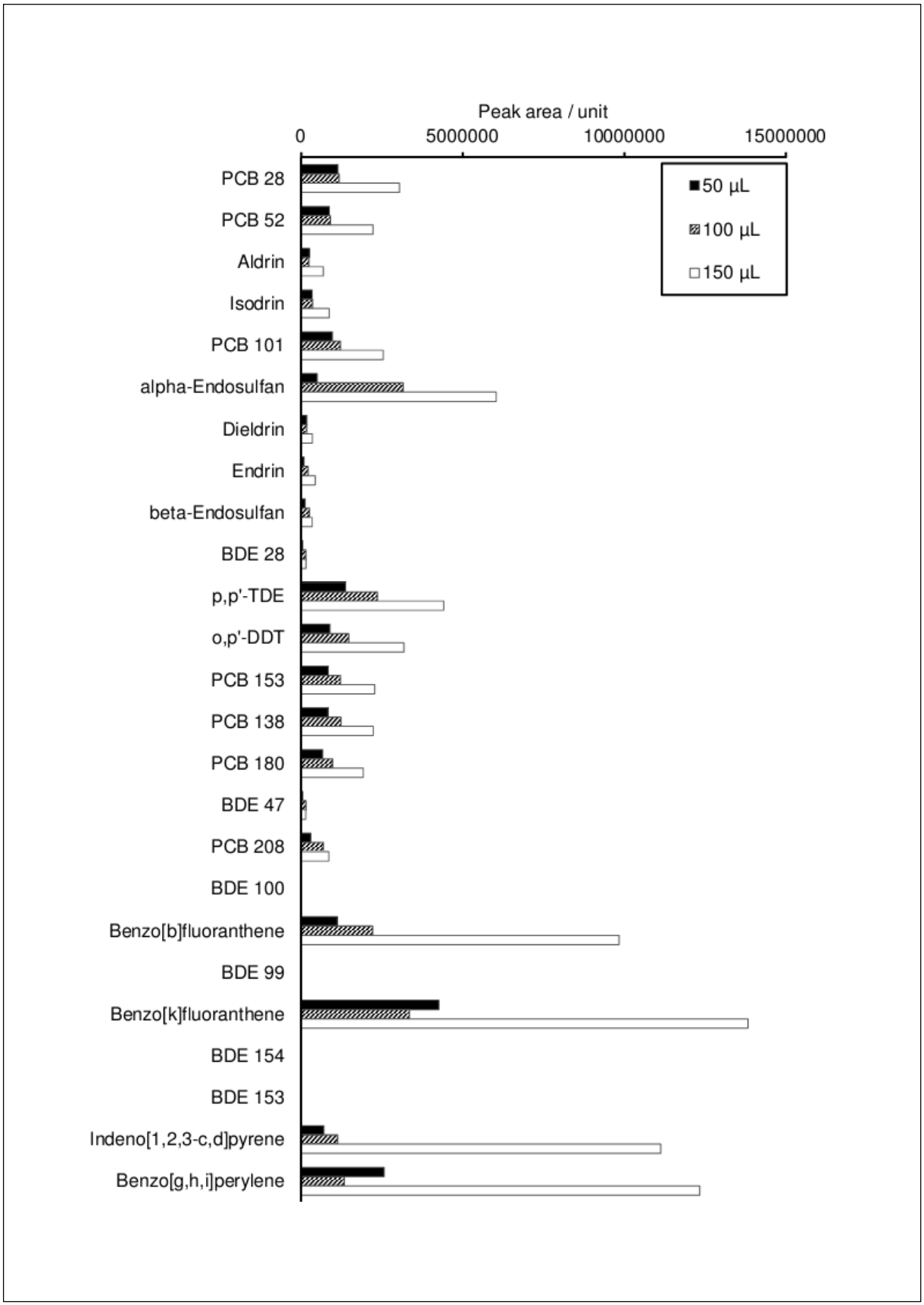

Figure 7.5: Variation of the injection volume during the method development at a purge time of 2 min

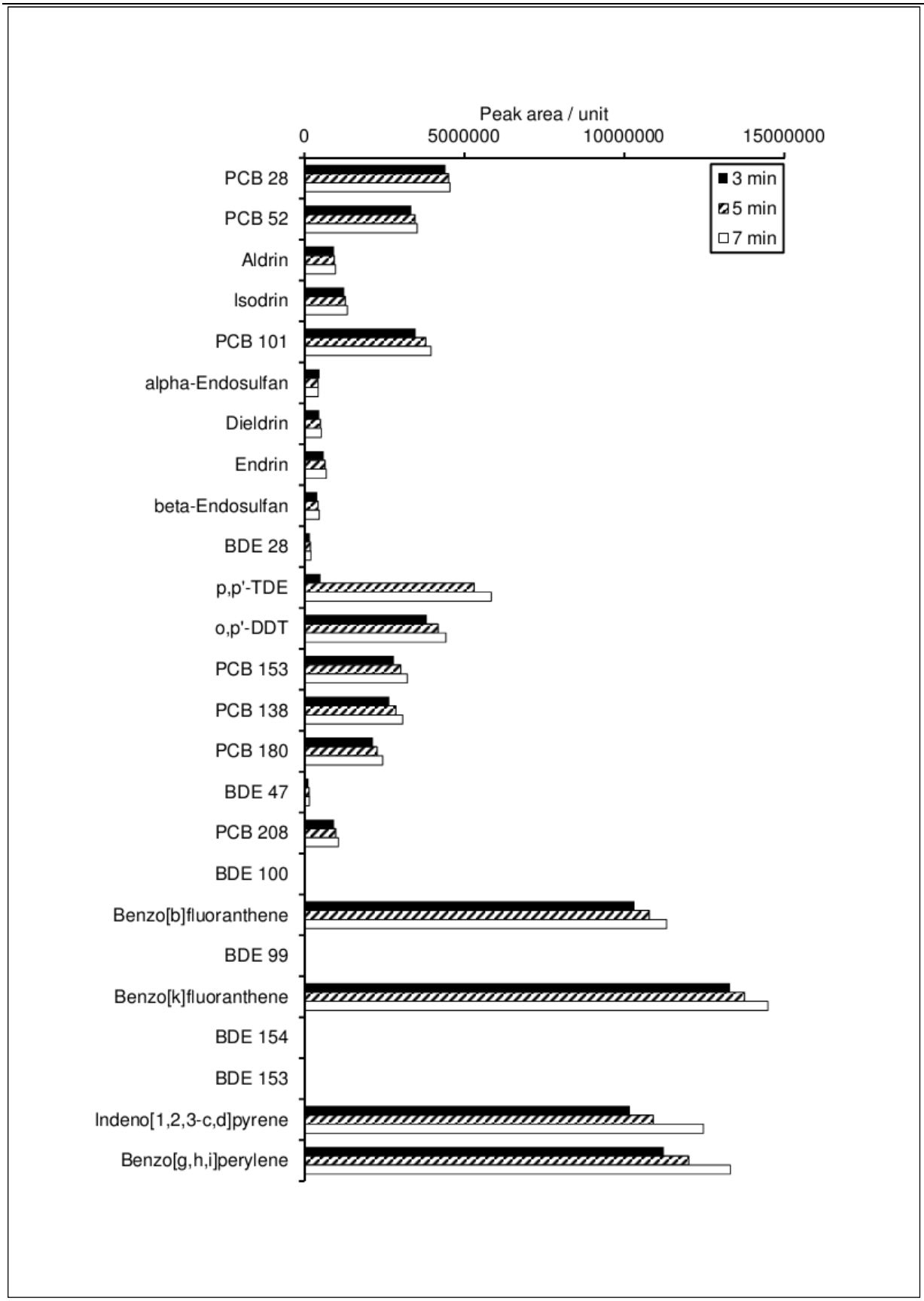

Figure 7.6: Variation of the purge time during the method development at an injection volume of 175 µL

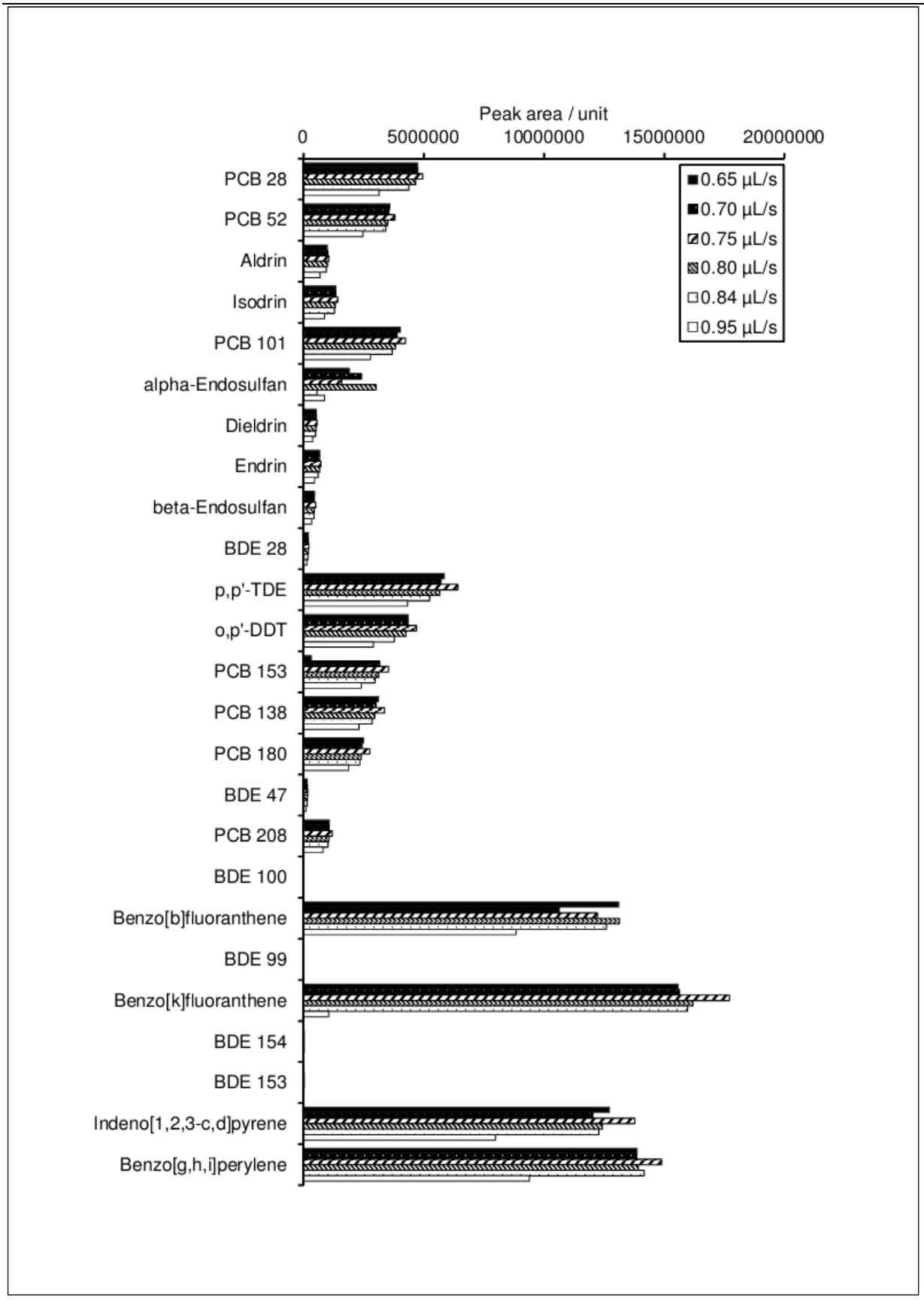

Figure 7.7: Variation of the injection speed during the method development at an injection volume of 175 µL

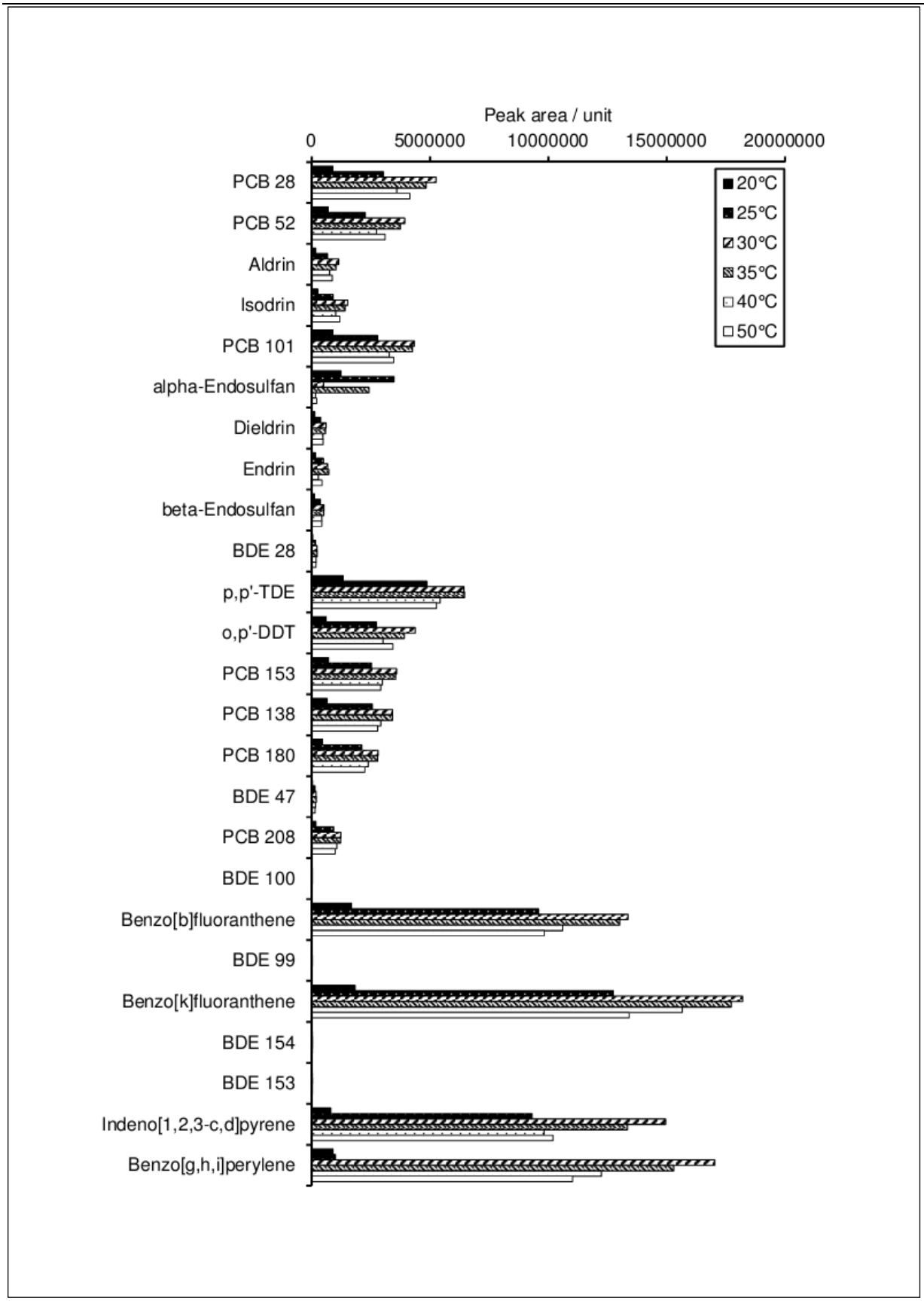

Figure 7.8: Variation of the injection temperature during the method development at an injection volume of 175 µL

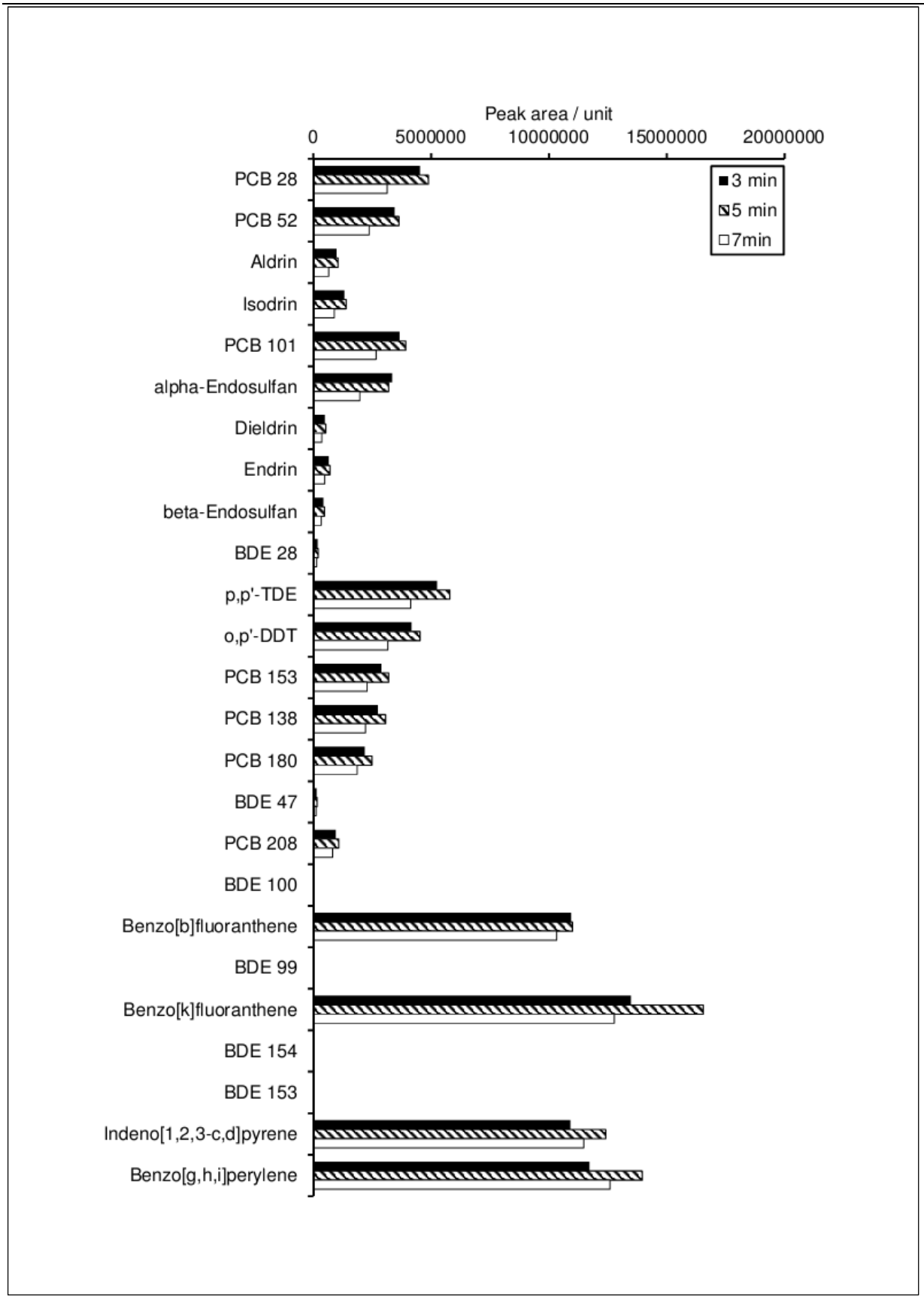

Figure 7.9: Variation of the holding time of the temperature at the end of CIS programme during the method development at an injection volume of 175 µL

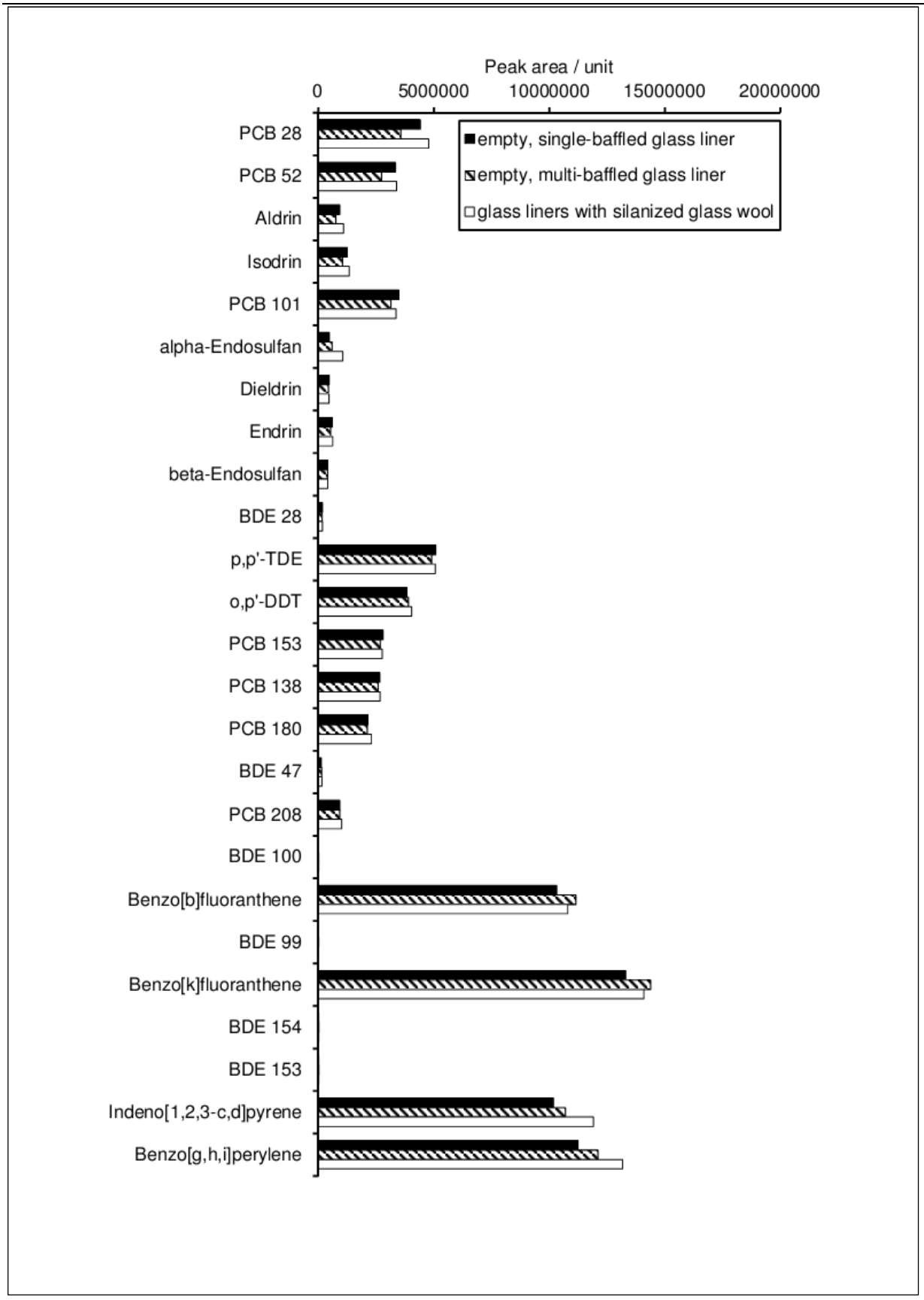

Figure 7.10: Variation of different liners during the method development at an injection volume of 175 µL

Some analytes are not clearly seen in Figure S1 to S6 caused by their low sensitivity. However, the peak area are high enough for quantification with about 10 000 units of area, which was corresponded to an analyte concentration in the water sample of 25 ng/L (Table S5, "Spike VII" solution) and was used for all LVI/GC-MS optimisation experiments.

7.5.3 Limit of determination and quantification

Table 7.14: Limits of determination (LODs) and quantification (LOQs) calculated by single to noise ratio (S/N) and DIN 32 645 [1] use k = 3 and a and b from the equation of calibration in the calibration range from 2.5 to 25 ng/L compared to the AA-EQS for inland waters of the Water Framework Directive (WFD) and German Oberflächengewässerverordnung (OGewV)

Substance	S/N = 6:1	Blank value method		Calibration method		AA-EQS	
	LOD	LOD	LOQ	LOD	LOQ	WFD [2]	OGewV [3]
	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
PCB 28	0.2	0.3	1.0	18	53	-	0.5[f]
PCB 52	0.2	0.4	1.2	873	2619	-	0.5[f]
Aldrin	0.2	0.2	0.51	34	102	10[a]	10[a, g]
Isodrin	0.4	0.7	2.2	39	118	10[a]	10[a, g]
PCB 101	0.6	1.1	3.1	27	80	-	0.5[f]
alpha-Endosulfan	0.9	6.5	19	35	104	5	5[g, h]
Dieldrin	1.8	3.0	9.0	27	82	10[a]	10[a, g]
Endrin	1.1	1.9	5.6	41	123	10[a]	10[a, g]
beta-Endosulfan	0.3	4.7	14	35	106	5	5[g, h]
BDE 28	0.1	2.5	7.6	23	68	0.5[b]	0.5[g]
p,p'-TDE	1.8	2.2	6.5	23	68	25[c]	25[c, g]
o,p'-DDT	1.2	0.5	1.4	80	240	25[c]	25[c, g]
PCB 153	1.5	2.3	7.0	24	73	-	0.5[f]
PCB 138	1.5	1.5	4.6	26	78	-	0.5[f]
PCB 180	1.4	5.8	17	11	34	-	0.5[f]
BDE 47	4.7	5.1	15	7.6	23	0.5[b]	0.5[g]
BDE 100	10	17	51	29	87	0.5[b]	0.5[g]
Benzo[b]fluoranthene	12	5.6	17	65	195	30[d]	30[g, i]
BDE 99	13	19	56	35	104	0.5[b]	0.5[g]
Benzo[k]fluoranthene	12	3.4	10	63	188	30[d]	30[g, i]
BDE 154	24	-	-	-	-	0.5[d]	0.5[g]
BDE 153	8	3.6	11	63	188	0.5[d]	0.5[g]
Indeno[1,2,3-c,d]pyrene	14	21	63	137	412	2[e]	2[g, i]
Benzo[g,h,i]perylene	15	15	48	133	399	2[e]	2[g, i]

-: not determinable or no information available

Table 7.15: Comparison of limits of quantification (LOQs) with LOQs mentioned in the literature of LVI methods combined with sample preparation procedures in water analysis

Substance	LOQ S/N = 10:1 ng/L					
	presented method SPE (disk)	[4]	[5]		[6]	
			SPE (cartridge)	MEPS	MASE	SBSE
PCB 28	0.3	-	22.1	15.3	-	-
PCB 52	0.3	-	68.8	12.3	-	-
Aldrin	0.4	166	-	-	-	-
Isodrin	0.6	-	-	-	-	-
PCB 101	1.0	-	99.0	8.3	-	-
alpha-Endosulfan	1.5	66	-	-	-	-
Dieldrin	3.0	66	-	-	-	-
Endrin	1.8	66	-	-	-	-
beta-Endosulfan	0.6	66	-	-	-	-
BDE 28	0.1	-	-	-	0.1	0.2
p,p'-TDE	2.9	-	-	-	-	-
o,p'-DDT	2.0	-	-	-	-	-
PCB 153	2.5	-	97.4	10.7	-	-
PCB 138	2.6	-	83.9	8.3	-	-
PCB 180	2.3	-	43.4	9.2	-	-
BDE 47	7.8	-	-	-	0.4	0.1
BDE 100	17	-	-	-	3.3	2.7
Benzo[b]fluoranthene	19	-	1.0	0.9	0.4	4.7
BDE 99	21	-	-	-	2.2	1.8
Benzo[k]fluoranthene	20	-	2.2	1.3	0.5	2.5
BDE 154	40	-	-	-	9.1	4.7
BDE 153	14	-	-	-	8.7	5.9
Indeno[1,2,3-c,d]pyrene	23	-	0.5	1.4	7.5	14.0
Benzo[g,h,i]perylene	24	-	0.2	0.8	10.3	7.5

-: no information available, SPE: solid phase extraction, MEPS: microextraction by packed sorbent, MASE: membrane-assisted solvent extraction

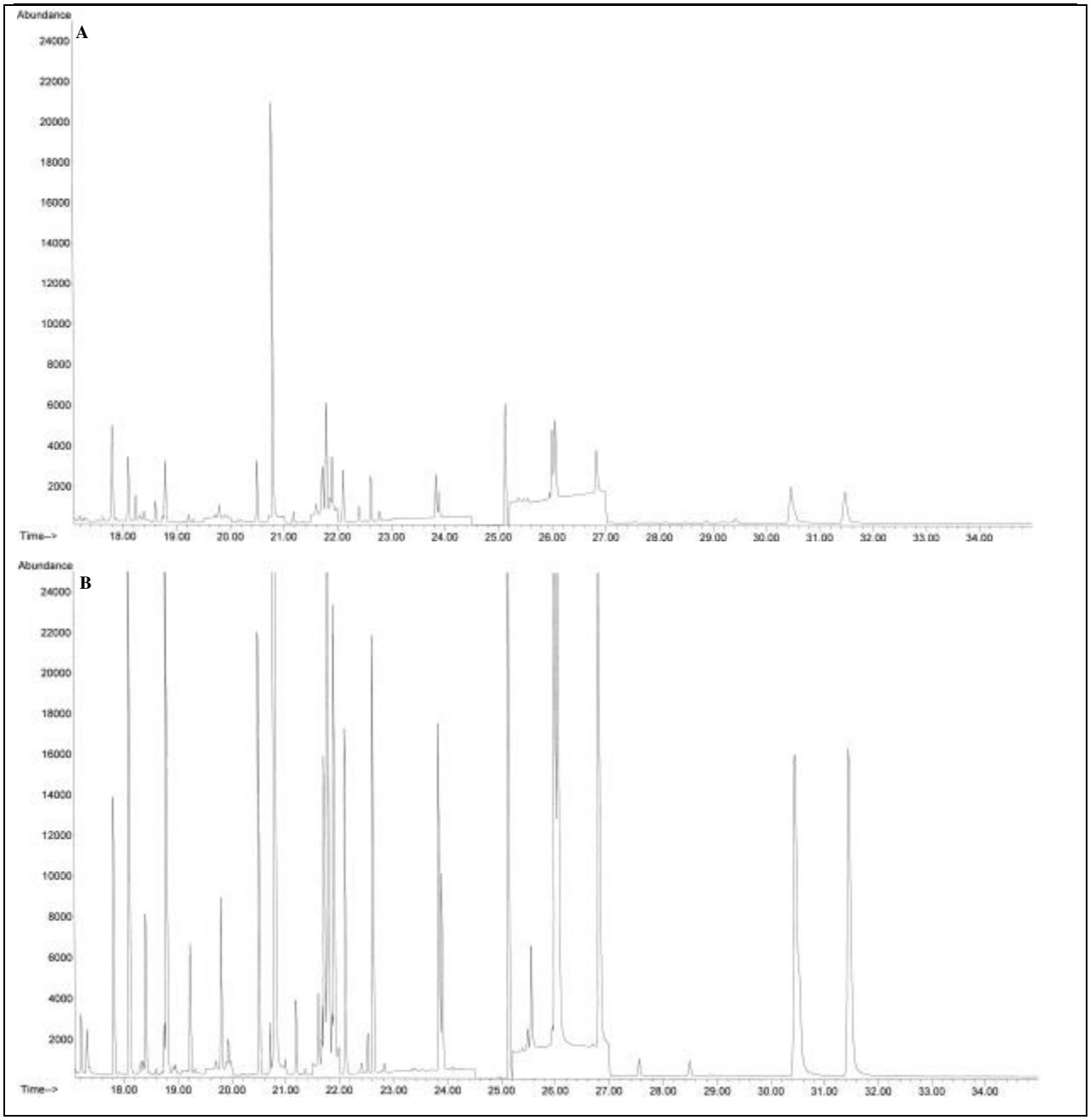

Figure 7.11: Total ion current chromatograms of a concentration of 2.5 ng/L analytes in the water sample in selected ion monitoring mode considering (A) with and (B) without SPE sample preparation

Table 7.16: Equation of calibration (y = b • x + a) and the belonging correlation coefficient (r) for analyte spiked blank water samples

Calibration range	0.25–2.5 ng/L			2.5–25 ng/L			LOQ-25 ng/L		
Substance	a	b	r	a	b	r	a	b	r
PCB 28	-1746.36	69851.25	0.9848	-37236.86	67309.82	0.9993	-15266.70	62950.27	0.9972
PCB 52	307.88	46628.11	0.9825	-45416.49	47532.24	0.9991	-15620.31	46045.90	0.9985
Aldrin	-1155.07	13149.69	0.9985	-8693.40	10653.16	0.9971	-1975.24	10284.42	0.9966
Isodrin	-11440.23	24218.82	0.9939	11429.21	13087.04	0.9992	-4576.50	18218.00	0.9983
PCB 101	-29906.48	66381.99	0.9587	14757.17	50762.43	0.9969	-4819.20	51771.97	0.9980
alpha-Endosulfan		< LOQ		927.49	9057.15	0.9897	6588.00	9525.78	0.9941
Dieldrin		< LOQ		-3262.11	10709.64	0.9995	-3262.11	10709.64	0.9995
Endrin		< LOQ		-4392.38	10253.38	0.9991	-355.68	10299.40	0.9961
beta-Endosulfan	-5279.49	12184.30	0.9341	2076.20	10038.21	0.9997	4290.11	7715.59	0.9964
BDE 28	7659.85	16191.80	0.9793	3192.06	22471.23	0.9964	-993.57	22686.88	0.9975
p,p'-TDE		< LOQ		60275.25	109438.97	0.9904	32201.88	110860.19	0.9915
o,p'-DDT		< LOQ		-7887.33	8273.05	0.9987	-4385.68	8113.75	0.9978
PCB 153		< LOQ		20980.06	41460.46	0.9951	17678.70	41625.90	0.9958
PCB 138		< LOQ		33968.63	40482.12	0.9934	28333.39	40764.53	0.9943
PCB 180		< LOQ		41794.94	29105.90	0.9912	26676.88	29319.32	0.9971
BDE 47		< LOQ		53505.73	21429.35	0.9922	53505.73	21429.35	0.9922
BDE 100		< LOQ		411.80	651.53	0.9891	411.80	651.53	0.9891

Table 7.16: Equation of calibration (y = b • x + a) and the belonging correlation coefficient (r) for analyte spiked blank water samples (continued)

Calibration range	0.25–2.5 ng/L			2.5–25 ng/L			LOQ-25 ng/L		
Substance	a	b	r	a	b	r	a	b	r
Benzo[b]fluoranthene	< LOQ			301397.54	120665.65	0.9217	301397.54	120665.65	0.9217
BDE 99	< LOQ			1090.85	397.53	0.9791	1090.85	397.53	0.9791
Benzo[k]fluoranthene	< LOQ			546331.51	205798.74	0.9822	546331.51	205798.74	0.9822
BDE 154	< LOQ			< LOQ			< LOQ		
BDE 153	< LOQ			-11032.74	2095.80	0.9393	-11032.74	2095.80	0.9393
Indeno[1,2,3-c,d]pyrene	< LOQ			249931.94	133454.29	0.9941	249931.94	133454.29	0.9941
Benzo[g,h,i]perylene	< LOQ			154703.68	111320.86	0.9883	154703.68	111320.86	0.9883

LOQ: limit of quantification, < LOQ: calibration range is smaller as the LOQ or less than four calibration points

7.5.5 References

[1] DIN 32 645 "Nachweis-, Erfassungs- und Bestimmungsgrenze - Ermittlung unter Wiederholbedingungen - Begriffe, Verfahren, Auswertung" (Mai 1994).

[2] Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council (2008).

[3] Verordnung zum Schutz der Oberflächengewässer (Oberflächengewässerverordnung - OGewV), Bundesgesetzblatt Teil 1, Nr. 37 (25 July 2011).

[4] S.H.G. Brondi, F.C. Spoljaric, F.M. Lancas, J. Sep. Sci. 28 (2005) 2243.

[5] A. Prieto, S. Schrader, M. Moeder, J Chromatogr A 1217 (2010) 6002.

[6] A. Prieto, O. Telleria, N. Etxebarria, L.A. Fernandez, A. Usobiaga, O. Zuloaga, J. Chromatogr., A 1214 (2008) 1.

7.6 General conclusions and outlook

No supplements.

7.7 List of publications

Publications in peer-reviewed journals

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
Determination of organic priority pollutants in the low ng/L-range in water by solid phase extraction disk combined with large volume injection/gas chromatography-mass spectrometry
Analytical and Bioanalytical Chemistry, **405** (2013), 5215-5223.

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
Multi-component trace analysis of organic xenobiotics in surface water containing suspended particular matter by solid phase extraction/gas chromatography-mass spectrometry
Journal of Chromatography A, **1249** (2012), 181-189.

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
Occurrence of residual water within disk based solid phase extraction and its effect on GC-MS measurement of organic extracts of environmental samples
Analytical and Bioanalytical Chemistry, **303** (2012), 2541-2552.

Other Publications

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
Multikomponentenmethode zur Bestimmung von 54 organischen Xenobiotika in schwebstoffhaltigen Oberflächengewässern mittels SPE-GC/MS
Vom Wasser – Das Journal, **109** (2011) 2, 37-39.

Oral presentations

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
Determination of the 16 EPA PAHs in surface water containing suspended particulate matter using SPE disks followed by GC-MS
Münster (Germany), 23rd International Symposium on Polycyclic Aromatic Compounds (ISPAC 23), September 4 – September 8, 2011.

Poster presentations

C. Erger, T. C. Schmidt:
Untersuchung von Transformationsprodukten bei der Ozonung von Wasser kommunaler Kläranlage mittels SPE/GC-MS
Goslar (Germany), „Wasser 2013“ – Jahrestagung der Wasserchemischen Gesellschaft, May 5 – May 8, 2013.

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
Determination of 54 Organic Xenobiotics in Water containing Suspended Particulate Matter by a SPE/GC-MS Procedure
Goslar (Germany), „Wasser 2013“ – Jahrestagung der Wasserchemischen Gesellschaft, May 5 – May 8, 2013.

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
Determination of 54 Organic Xenobiotics in Water containing Suspended Particulate Matter by a SPE/GC-MS Procedure
Essen (Germany), ANAKON 2013, March 04 – March 07, 2013.

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
SPE-LVI/GC-MS method for the determiniation of organic xenobiotics in surface water
Neu-Ulm (Germany), „Wasser 2012“ – Jahrestagung der Wasserchemischen Gesellschaft, May 14 – May 16, 2012.

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
SPE/GC-MS Verfahren zur Bestimmung von 54 organischen Xenobiotika in schwebstoffhaltigen Oberflächenwässern
Langenau (Germany), Langenauer Wasserforum 2011, November 6 – November 7, 2011 (poster award).

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
Determination of 54 Organic Xenobiotics in the Whole Water Sample by SPE-GC/MS Considering the Water Framework Directive
Aachen (Germany), Workshop-Proceedings Processes in the Yangtze River System - Experiments and Perspectives, November 27 – November 29, 2011.

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
Multikomponentenmethode zur Bestimmung von 54 organischen Xenobitika in schwebstoffhaltigen Oberflächengewässern mittels SPE-GC/MS
Norderney (Germany) „Wasser 2011“ – Jahrestagung der Wasserchemischen Gesellschaft, May 30 – June 1, 2011 (incl. short oral presentation).

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
Determination of 54 Organic Xenobiotics in the Whole Water Sample by SPE-GC/MS Considering the Water Framework Directive
Zürich (Switzerland), ANAKON 2011, March 22 – March 25, 2011.

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
The Drying Process and its Influence on the Residual Water in Solid Phase Extraction Disks
Zürich (Switzerland), ANAKON 2011, March 22 – March 25, 2011.

C. Erger, P. Balsaa, F. Werres, T. C. Schmidt:
Determination of 52 organic compounds in the whole water sample by SPE-GC-MS considering the Water Framework Directive
Valencia (Spain), 28th International Symposium on Chromatography (ISC 2010), September 13 – September 16, 2010.

C. Erger, B. Herrmann, K. Steinbach:
Separation of TNT and its transformation products – a comparison between HPLC and MEKC
Münster (Germany), 27th International Symposium on Chromatography (ISC 2008) September 21 – September 25, 2008.

7.8 Curriculum Vitae

Der Lebenslauf ist in der Online-Version aus Gründen des Datenschutzes nicht enthalten.

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7.10 Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit mit dem Titel:

„Determination of priority organic substances in surface water containing suspended particulate matter by disk solid phase extraction"

selbst verfasst und keine außer den angegebenen Hilfsmitteln und Quellen benutzt habe, und dass die Arbeit in dieser oder ähnlicher Form noch bei keiner anderen Universität eingereicht wurde.

Essen, im Juni 2013

Christine Erger